The 17th Annual Waste Testing & Quality Assurance Symposium

PROCEEDINGS

August 12-16, 2001

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WTQA 2001

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Proceedings

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Waste Testing & Quality Assurance Symposium (WTQA 2001)

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Arlington, VA

HIGHLIGHTS

17th Annual Waste Testing & Quality Assurance Symposium (WTQA 2001)

Effective Environmental Information

This year we have expanded the technical sessions to bring you additional features in both our program and also our short courses. Special Issue Sessions include three Department of Defense sessions, Air Source Emissions Measurement and Monitoring, NELAC/ACIL technical issues, Field/New Technologies, Data Quality and Validation Under PBMS, and three sessions on EPA's Data and Information Quality Improvement. All of these are in addition to our regular featured sessions on organic and inorganic analyses and our poster sessions. In addition, the first NIST Workshop on Proficiency Test Studies will be held separate from, but in association with, WTQA 2001. Our short courses also reflect an expanded breadth of topics that range from a DoD course on Inappropriate Lab Practices to field and laboratory technologies that include organic mass spectrometry, solid phase extraction techniques, field analytical technology including the use of immunoassays, the new FORMS II Lite system, and RCRA analytical strategies. In addition, courses on assessor training, permit writing under PBMS, and PBMS training are offered. This strong and varied technical program is designed to help you learn about important changes and advances occurring in the field of environmental analytical chemistry. Join us and meet with the leaders who are shaping our future work.

Opening Reception Concurrent with Opening Table Top Exhibition
Monday, August 13, 2001; 5:00 - 7:00 pm

The opening reception follows the plenary session and is concurrent with the opening of the Table Top Exhibition. Join us for complimentary hors d'oeuvres and soft drinks to meet your fellow conferees, exhibitors, and EPA officials. A cash bar will also be available.

Special Sessions

This year we have more special sessions than ever before. They reflect the diversity and rapidly evolving changes in modern environmental sampling and analysis. Three sessions devoted to Department of Defense topics highlight the growing importance of environmental technology to this government agency. Two sessions covering new technologies, and highlighting field analyses, continue an expanded coverage of last year's popular topic. Two sessions on air source emissions and monitoring introduce a new topic for WTQA. Three sessions on EPA data and information improvements feature the continued quality assurance focus and are supplemented with another special session on data quality and validation under PBMS. A final special session focuses on the technical issues faced by NELAC. Supporting these special sessions are the inorganic and organic regular sessions that provide a continuing foundation for the conference.

Special sessions with invited speakers for oral sessions include:

- Data Information Quality Improvement;
- NELAC and ACIL Technical Issues Involving the National Environmental Laboratory Accreditation Program; and
- Data Quality and Evaluation Under PBMS in Department of Defense Programs.

Short course topics will include assessor training; using the DoD model to develop quality assurance

project plans; writing permits using the PBMS approach; the triad approach to streamlining site characterization/cleanup; designing more effective and cost-efficient sampling and analysis plans by using a mix of field and fixed lab measurements; using solid phase extraction (SPE) sample preparation procedures to reduce monitoring costs; identifying appropriate laboratory practices; taking advantage of the benefits the PBMS approach offers when using SW-846 for RCRA monitoring; and effectively employing analytical organic mass spectrometry techniques (including GC/-, LC/-, SFC/-, and CE/MS).

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A MANAGEMENT SYSTEM FOR INFORMATION QUALITY

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ABSTRACT

Quality management systems = *management systems for quality*.
When a chief product of an enterprise is information, ensuring the quality of that information becomes a priority for the enterprise. Managers need management systems which address quality of both production and distribution of the information. When some of the information resident in the information systems includes scientific measurements, the quality of the "content" is also a concern. This technical paper provides an overview of the issues for managers regarding information quality and proposes an approach to consider in developing and documenting a management system for information quality.

INTRODUCTION

The USEPA has developed quality systems which support the scientific method and the needed environmental measures to support decisions using the scientific method. The process of science produces a variety of information. Other processes in the Agency also produce information. One example is the regulatory and enforcement programs. As enterprises provide increasing access to all their information and as customers rely on computerized access to information via the Internet, the old approach to managing the information changes. Enterprises now identify information as a strategic resource. The method by which the quality of the information is managed also must change. New management systems for quality need to evolve to address all aspects of those processes which held to ensure the quality of the information including design of data, design of enterprise architectures, production processes for information, data warehousing, software and hardware, and distribution of information via web portals. The following sections describe considerations for reconciliation of terminology between the disparate disciplines involved in information quality and provide a plan and outline for development of management systems for information quality.

TERMINOLOGY

Current terminology in use in USEPA and other enterprises working in both scientific measurements and the quality of information in information systems may not be adequate to capture the concepts being discussed in management systems for information quality. For example, the term *data quality* has broad meaning and for a scientist may often refer to the quality of a scientific measurement or environmental measurement. This quality is often expressed in terms of *data quality indicators*. These data quality indicators are represented by additional data elements that are collected concurrently with environmental samples or determined during analytical procedures. These additional data elements (i.e., the data quality indicators) serve to provide meaning and value to the environmental measurements.

The term *data quality* is often used by the information science profession to indicate that data were entered into the computer information system correctly. This is obviously a different kind

of data quality.

One method to provide clarification is to provide more specific definitions of data quality and to frame a model of the different components of information quality using definitions. Part of the model is to divide up information quality into two key components:

- information production
- information distribution

The following definitions are offered describing key concepts for a management system for information including data, information, quality and systems, data quality, information quality, information production quality and information distribution quality. The works of both Larry English (English, 1999) and Thomas Redman (Redman, 1996) were critical resources in developing this list.

DATA DEFINITIONS

datum - (data item) is a *representative triple* which consists of **e, a, v** where

e = entity (and the entity's meaning)

a = attribute (and the attribute's meaning)

v = value (and the value's meaning). The value may include *units* when the datum represents a measurement. (Redman, 1996)

NOTES:

a. The datum represents some element in a model; the element is a real world thing (tangible = physical, intangible = e.g., idea) or event. As an event, the datum would need to be captured at the point of the event.
b. The datum usually represents a fact, a truth or an observation about the real world; but does not always have to represent a fact.

data representation - a set of rules for recording data (*representative triples*) on some medium

NOTES:

a. Therefore, the same data may be represented in different ways.
b. Therefore, data represented in a prescribed manner may be recorded many times.
c. Data can exist without being represented.
d. These rules are a form of "metadata" (Redman, 1996)

data record - a physical instance standing for a set of data items according to the data representation

NOTES:

a. Data can exist without being recorded. (Redman, 1996)

environmental data - data of measurements or observations that describe environmental processes or conditions, or the performance of environmental technology (ANSI/ASQC E4-1994)

NOTE: In a broader sense, these data may include ancillary data which are needed so that the data have meaning (are useful as *information*), data such as: name of the sample site, sample location, sample no., collection methodology, etc.

geospatial data - data of geospatial measures that include a three-dimensional reference

system (usually based on a model of the real world)
NOTE: Often the three-dimensional reference system is cross-referenced to observational data regarding a physical attribute for locations and is often considered to be *environmental data*.

quality indicator data - data of the quality indicators.
NOTES:
1. When associated with environmental measurements, this data is usually developed and recorded at the same time the measurements are developed and recorded.
2. This type of data is sometimes referenced as *meta-data*.

INFORMATION **DEFINITIONS**

information - a datum or data presented to meet customer expectations
NOTES
a. Data presentation must be knowledge worker friendly.
b. Data presentation must impart meaning to the data.

information production - that aspect of the information which is associated with the creating, updating, collecting and storing information that gives the information value to the stakeholder (vs. other aspects of the information such as the *data representation*)

information distribution - that aspect of information that is associated with the distribution (i.e., extraction, manipulation and presentation) of information.

information system - in the broadest sense, a system of functions concerning the acquisition and transfer of information. (Principia Cybernetica, 2000)
NOTES:
a. Carriers in an information system can be biological, social or personal units, etc.
b. An information system is dedicated to a certain type of information (e.g., environmental information.
c. A storage device is usually part of an information system.

QUALITY **AND** ***SYSTEMS*** **DEFINITIONS**

quality - the totality of *features* and *characteristics* of a product or service that bears on its ability to meet the stated or implied needs and expectations of the customer. (ANSI/ASQC E4-1994)

quality assurance (QA) - an integrated system of management activities involving planning, implementation, assessment, reporting and quality improvement to ensure that a process, item or service is of the type and quality needed and expected by the customer. (ANSI/ASQC E4-1994)

quality control - the overall system of technical activities that measures the attributes and performance of a process, item or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality. (ANSI/ASQC E4-1994)

quality feature - an individual feature of a product or service that is identified as a feature of interest for the purpose of a quality system.
NOTE: A quality feature may be subject to measurement (see *quality indicator)*.

quality indicators - measurable attributes of the attainment of the necessary quality (quality features). (ANSI/ASQC E4-1994)
NOTE: In USEPA, quality indicators originally were applied solely to the “quality" necessary for a particular environmental decision and included: *precision, bias, completeness, representativeness, reproducibility, comparability* and *statistical confidence*. OEI is identifying a greater breadth of quality indicators to describe and measure the quality of overall Agency information quality.

quality management - that aspect of the overall management system of the organization that determines and implements the quality policy. Quality management includes strategic planning, allocation of resources and other systematic activities (e.g., planning, implementation, assessment) pertaining to the quality system. (ANSI/ASQC E4-1994)

quality system - “the management system for quality” a structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability and implementation plan of an organization for ensuring quality in its work processes, products (items) and services. The quality system provides the framework for planning, implementing and assessing work performed by the organization and for carrying out required QA and QC. (ANSI/ASQC E4-1994)

management system - a structured non-technical system describing the policies, objectives, principles, organizational authority, responsibilities, accountability and implementation plan of an organization for conducting work and producing items and services. (ANSI/ASQC E4-1994)

***DATA QUALITY* DEFINITIONS**
data quality - the totality of features and characteristics of data that bear on its ability to meet the stated or implied needs and expectations of the customer.
NOTE: One narrow definition of data quality is
“data quality = data representation quality + data record quality”

data representation quality - attributes of data representation quality include:
- the rules for recording data provide data meet the customer’s definition
- the format allows for processing by explicit procedures
- the format allows data to retain its characteristics during repeated use

data record quality - attributes of data record quality include:
- the record is a true record of the element that was meant to be recorded (special cause bias)
- the record was accurately recorded (freedom from common cause bias; e.g., systematic data entry error)

data standards quality - the degree to which the data standards enable people to easily define data completely, consistently, accurately and understandably. (English, 1999)

data architecture quality - the degree to which the data models are reused, stable and flexible and how well they depict the data requirements of the enterprise; and how well the databases implement those requirements and enable capture, maintenance and dissemination of the data among the information customers. (English, 1999)

***INFORMATION QUALITY* DEFINITIONS**

information quality - the quality of the information production + the quality of the information distribution (see following sections)

***INFORMATION PRODUCTION* QUALITY DEFINITIONS**

information production quality - the totality of features and characteristics of information production that bears on its ability to meet the stated or implied needs and expectations of the customer.

(environmental) measurement quality - the quality indicators that describe the (inherent) quality of environmental measurement results. These include *precision, bias, completeness, representativeness, reproducibility, comparability* and *statistical confidence*.

information verification and validation - the degree to which the information has been verified and validated and show to meet requirements related to development of the data (e.g., analytical methods validation)

***INFORMATION DISTRIBUTION* QUALITY DEFINITIONS**

information distribution quality - the totality of features and characteristics of information distribution that bears on its ability to meet the stated or implied needs and expectations of the customer. (e.g., *data entry quality*, *data warehouse quality*, *information architecture quality*, etc.)

date entry quality - those quality features that describe quality related to the data entry process (e.g., *correctness*, *completeness, data entry verification*)

data warehouse quality - those quality features that describe the quality of data resident in Agency data warehouses (e.g., *duplicate data entry, completeness*)

information architecture quality - the degree to which information models are reused, stable and flexible and how well they depict the information requirements of the enterprise (e.g. *non-redundant system processes*, *business information model clarity*, *operational data model clarity*) (English, 1999)

software quality - those quality features of the software that ensure that the software meets the data and operational requirements of the stakeholders and ensures the quality of the information managed and delivered by the software. (e.g., *verified software*, *validated software*, *conformance of software to enterprise requirements*)

hardware quality - those quality features of the hardware that ensure that the hardware meets the requirements of the stakeholders and ensures the quality of the information managed and

delivered by the hardware (e.g., *reliability*, *maintainability*)

information usability - the degree to which information is usable for its intended purposes.

CONFUSING TERMINOLOGY

Some terms are used in regards to information and data. There terms may have vague meanings or different meaning to different parties. They include:

term	**potential meaning in *environmental science***	**potential meaning in *information technology***
data integrity	*potential synonym for "quality"*	*conformance to technical criteria and business rules*
reliable data	*data were generated by a reputable source and are of the quality needed*	*data are correct and have been securely maintained*

WHAT IS THE DIFFERENCE BETWEEN DATA QUALITY AND INFORMATION QUALITY?

The difference between the two terms is provided clearly in the definitions above; however, the biggest issue in regards to these terms is that people do not routinely distinguish between these two terms as defined in this technical paper. They are often treated as synonyms. The best approach when discussing information quality and data quality with another party is to be sure to share your definitions of the terms that you are using. This will help remind each party to be more specific in the discussion.

REVIEW OF AGENCY GUIDANCE

Quality guidance The USEPA established formal quality policy in 1980 and re-affirmed the policy in 2000 in USEPA Order 5360.1 A1 and USEPA Order 5360.1 A2, USEPA Quality Manual. These documents provide for the quality of the environmental measurements; however, guidance development in the specific area of information quality is left to each office to develop relative to their own work efforts and outputs. This guidance is available at www.epa.gov/quality.

Information guidance Various information system guidance is available for the development of software and hardware maintenance. Information Resources Management (IRM) Policy, Standards, Guidance & Planning Documents are available at www.epa.gov/irmpoli8/.

REVIEW OF EXTERNAL GUIDANCE

External guidance and standards are also available covering both quality management systems and information systems. ANSI/ASQC E4-1994, *Specifications and Guidelines for Environmental Data Collection and Environmental Technology Programs* is available from the American National Standards Institute (ANSI) or the American Society for Quality (ASQ). This standard forms the basis for the USEPA quality manual; however, there is minimal guidance for information quality. ANSI site is www.sei.cmu.edu/. ASQ site is www.asq.org. The Software Quality Division of the ASQ also maintains a website www.asq-software.org/.

The Institute of Electrical and Electronic Engineers (IEEE) offers a variety of standards applicable to information systems including quality system guidance available at

www.ieee.org. The International Organization for Standardization (ISO) offers both standards and guidance for quality systems and for specific information technology applications available at www.iso.ch. The SPICE initiative to develop an International Standard for Software Process Improvement offers some interesting guidance available at www.sqi.gu.edu.au/spice/. The Software Engineering Institute (SEI) promotes use of the Capability Maturity Model (CMM) for information systems development. Their site is www.sei.cmu.edu/.

WHAT IS UNIQUE ABOUT DATA QUALITY AND INFORMATION QUALITY AT EPA?

Scientific measures As previously discussed, the USEPA's information includes scientific measurements. Because scientific measures often include *data quality indicators*, workers must be clear in their communications about what aspect of information quality they are discussing when discussing these data.

External data sources The sources for data in the Agency's data systems might not be the Agency. Many data elements may be entered directly by States, regulated entities or other outside parties.

Comparability of data in different systems The same kind of data found in different systems might not be readily comparable because the data were recorded using different minimum requirements; for example, the data may have come from different programs.

Understanding what may be unique about the data and information in any system is important when developing management systems for information quality.

DESIGNING A MANAGEMENT SYSTEM FOR INFORMATION QUALITY

In order to design a management system for information, managers need to:

Establish basic quality system needs The basic components of quality systems are the same whether manufacturing widgets, collecting scientific information or developing information technology. These basic components are identified in both Agency guidance and in ISO 9000 series of quality management standards. They include things such as management and organization, roles and responsibilities, training, inspection, etc. These are expressed in detail in the following suggested formats.

Identify key processes which require systematic management The key processes are dependent upon the operations of the individual enterprise. For the model suggested here, the enterprise is involved in both scientific measurement and development of delivery systems (information technology and software) for the information.

FORMATTING THE WRITTEN QUALITY SYSTEM

A three-tiered model is suggested based on the ISO 9000 style of quality system. The following are suggested approaches for each element of the management system for quality.

High-level elements (top tier, tier I)

This tier needs to include both the vision and mission statement of the enterprise. If these do not already exist, managers and quality managers may need to develop them. Following is

some guidance:

- **Vision** - the vision statement should be forward looking and include some statement of expectation that will be achieved in a certain time frame.
  To be the best _____ and to be recognized as such by customers as well as peers in the industry in the next 10 years.
- **Mission** - the mission statement should be a description of the individual things that must be accomplished in order to fulfill the vision.

This top tier also needs to include a quality policy statement:

- **Quality policy statement** - the quality policy statement should provide a clear indication of management's commitment to their hopes for the quality of the products of the enterprise. This statement should reflect their approach to the quality system.

General description (tier I)

The general description of the management system for information quality identifies key elements for planning implementation and assessment. The purpose of this section is to provide a story of how quality is accomplished in the enterprise which can serve as a summary of the system. Including the following tables in the general description will draw attention to quality management commitments in the following areas:

- **roles and responsibilities** - identification of management and quality management roles cross-referenced to activities critical to quality system development (resource commitment, quality system records, assessment schedule, training, quality records, procurement, etc.)
- **quality system records** - record type (quality plan, quality reports, etc.) cross-referenced to responsibilities for preparation, review, approval, frequency of development and distribution
- **quality assessment schedule** - assessment types (e.g., project, product, system, quality system, data system, etc.) cross-referenced to assessment tool, assessors, basis for assessment, minimum frequency, purposes for assessment and review authority

Quality Policies & Procedures (tier II)

Tier II includes the quality policies and procedures of the organization. These are akin to administrative policies and procedures that the enterprise may already have developed for routine administration. For each unique activity, an individual statement of quality policy for each key area of the information quality system as well as higher level procedures. This approach will allow for future editing to the overall quality manual for a single quality area without re-drafting the entire overall document. For each individual quality policy, include the following elements at a minimum:

- policy title
- approval authority and date
- succinct policy statement
- individual statement of quality requirements (if greater detail is needed)
- purpose
- scope
- responsibility and the role for implementing that responsibility
- listing of any associated documents

- procedures
- quality control (checklist) items that must be addressed

The following are the specific recommended topics for individual information quality policies and procedures:

general quality system

1. quality management system and plan
2. quality system roles and responsibilities
3. quality program resources
4. quality program documents and records
5. quality system dispute resolution
6. quality improvement

information quality

1. information and data quality approach
2. identification and categorization of information quality characteristics

assessments

1. system assessments
2. program/project assessments
3. product inspections
4. technical document assessments

training

1. personnel qualifications and training

customers

1. customer satisfaction performance standards

suppliers

1. procurement of items and services

products

1. program quality planning
2. project quality planning
3. other product (as defined by the enterprise)

information technology

1. data standards
2. information architecture
3. software quality
4. hardware quality
5. data warehouse quality
6. data stewardship
7. quality control inspections

Guidance Section - a shopping list of information quality criteria (level II addendum)
An addendum to the policies and procedures may be a listing of all applicable information quality criteria (e.g., completeness, correctness, timeliness, etc.) associated specifically with the general activity (e.g., data design, data warehouse, scientific measure, etc.). This list can serve as a shopping list for the project managers when they are planning the projects and need assistance in identifying application information quality indicators. This section has been developed for the USEPA Office of Environmental Information. An electronic copy of this is available in Wordperfect format from the author; please send an email if you would like a copy.

Checklist Section (level II addendum)
Another useful section to include when developing a management system for information quality is a checklist that will be used to verify conformance to each quality policy and procedure. If this checklist addendum is developed at the same time as the policies and procedures, the authors of the document will be encouraged to develop a system that is easily assessed.

Standard Operating Procedures (level III)
Tier three consists of the individual SOPs of the enterprise or each unit in the enterprise. SOPs are the actual work instructions for performing individual activities and are subject to frequent change. SOPs should be written in a way which facilitates their use and each modification for improvement.

SUMMARY
Successful development and implementation of a management system for quality is dependent on a clear understanding of both quality systems and information systems. Developing a modular system addressing quality policies and procedures for all activities associated with quality of products and information systems will facilitate quality improvements.

THE QUALITY LIFE CYCLE FOR SCIENTIFIC INFORMATION

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ABSTRACT

The USEPA has continued to focus quality planning in the important areas of environmental measurement, environmental technology and secondary use of the existing environmental measurement data. Expanded methods to communicate with agency customers via the Internet and the option to provide not only information, but also tools for viewing and manipulating that information require a new understanding of the quality principles which ensure the production and delivery of information.

Enterprises which value information as a strategic resource need a model to understand the processes which impact the production and development of information and consequently, the *information quality.* This technical paper presents such a model: a *quality life cycle* for information based on the concept of a *value chain* and applies the concept to the major data types in environmental measurements data systems and related systems.

INTRODUCTION

Production and delivery of information has always been a priority of Federal agencies. Prior to computer utilization, agencies had robust systems based on paper formats. These paper-based systems did not easily allow for ready retrieval of the information or readily allow for amalgamation of disparate data in efforts to identify interrelationships. Computers and database systems offered additional ability to study data results and began to serve as repositories of larger and larger sets of data. For the EPA, much of this data represented environmental measurements. Rapid advances in computing and the growth of the Internet changed the methodology by which Federal agencies interacted with their customers and persons working with the data.

Many current quality systems models deal primarily with information production processes related to decision-making, which usually include environmental measurements. Customer expectations for the agency's product has evolved to include rapid delivery and tools to manipulate a wide array of information types.

Agency customers now ask questions such as:

- Is the information reliable?
- What is the quality of this information?
- How do you ensure the integrity of the information?

These questions are often broad in scope and because there is not a standard lexicon for a

discussion of *information quality*, customers may have a difficult time framing their specific concerns regarding overall *information quality* or the quality of individual aspects of information quality.

Quality managers need an information model based on a quality perspective which allows for easy understanding in order to facilitate appropriate quality planning and implementation. This technical paper discusses the *value chain* concept and applies the concept to Agency data types. The resulting model allows for identification of key activities, major characteristics and specific information quality indicators. But first a story.....

THE BLIND MEN AND THE ELEPHANT The parable of the blind men and the elephant is credited to both Hindu and Islam folk tales. In this famous parable, six blind men have the occasion to meet up with an elephant. Each man in turn touches a different part (legs, tail, trunk, tusks, ears) and announces his evaluation of the elephant as being tree-like, wall-like, fan-like, snake-like and rope-like. Of course, the moral of the story is that you cannot comprehend an elephant just by looking at one of its parts AND an elephant is more than the sum of its parts.

Likewise, *information quality* challenges are addressed by different disciplines as various types of problems. Scientists view the challenge as the need for better implementation of quality principles and science during technical operations such as environmental measurements. Software developers view the challenge as the need for better data/functional definitions and requirements. Database managers view the challenge as the need for better information collection and more complete and correct data in the data system. Web site managers view the challenge as the need for better web design and understanding of customer requirements. Planners view the challenge as the need for better metadata requirements and standard data architecture. Customers and the public working with the data view the challenge as more focus on customer needs and an expanded view of additional possible uses of measurement data.

INFORMATION AS THE ELEPHANT

Similar to viewing the elephant, viewing *information quality* requires comprehension of all the individual parts (processes and activities) as well as how the parts interact. Professionals in science, technology and information may sometimes act as individuals “blind” to the action of

other individuals who can impact *information quality*. Besides the lack of an effective model, many professionals use wholly different lexicons when referring to data. Changing the lexicon is not the purpose of a model, but a model can help standardize some terminology.

Recognition of all individual components is very important to understanding *information quality* because it is through breaking down the "big picture" into its individual components that an individual can view the contribution of each component to the whole. This also allows an individual to recognize similarities and differences related to the individual components. In some cases, each component may contribute to an overall information quality *characteristic* such as *completeness*. In other cases, each component may have an information quality characteristic, such as *unnecessary duplicates*, that is unique to the activity of database management.

WHAT IS A *VALUE CHAIN*?

Michael Porter of the Harvard Business School introduced the concept of the *value chain* in the book Competitive Advantage: Creating and Sustaining Superior Performance (Free Press, 1985). A value chain is a model for an enterprise encompassing all steps in the production of a product, from raw materials through finished products to the customer. General business, industry and e-business have all adopted versions of the concept as a planning tool.

A key feature of a *value chain* is that the chain extends across all organizational boundaries of an enterprise. This approach allows planners to look at the activities which directly impact the subject of interest and not administrative aspects which make up the formal divisions in an enterprise. Readers interested in the concept of *value chain* can find significant information available on the internet.

APPLYING THE *VALUE CHAIN* TO QUALITY?

The concept of quality management fits particularly well with the concept of a *value chain*. The individual activities that form each link in the chain are the same processes which provide quality (value) or add value to the product as it moves along the value chain. These value-added features can be considered to be the *information quality characteristics* which added together form the overall understanding of *information quality*.

There are some key concepts that are related to the *information quality value chain*. It is important to distinguish these other models to avoid confusion.

PDSA (or PDCA) Shewhart Cycle

The plan-do-study-act (or plan-do-check-act) cycle was originally developed by Walter Shewhart (a mentor of Dr. William Edwards Deming) prior to 1939. This cycle focuses on the need to develop proper planning, implement work according to the planning, and then perform an assessment to evaluate both process efficacy and quality of the resulting product. The final step, "act," is the "assurance" in *quality assurance*. This critical process is related to the scientific method and is reflected in the quality planning documents (Quality Manual, R-5, etc.) of the USEPA. This process is distinct from the *information quality value chain* because this cycle may be performed for each activity (link) in the chain. For example, for field sampling and analytical analysis, this process occurs as a complete cycle prior to delivery of the resulting data to another link (e.g., information collection) in the chain.

Resource life cycle

Larry English describes the *resource life cycle* in his book Improving Data Warehouse and Business Information Quality: Methods for Reducing Costs and Increasing Profits (Wiley & Sons, 1999). He describes the following five processes required to manage any resource (people, money, facilities, equipment, materials, products and information).

- plan the resource
- acquire the resource
- maintain the resource
- dispose of the resource
- apply the resource

USEPA recognizes its information as a *strategic resource* of the enterprise. Information must then be managed as a resource. There are three unique aspects of information as a resource:

1. Information does not get used up. (but it can become obsolete)
2. Information can be copied
3. Information can be employed for applications that were not planned for when the information was developed.

This life cycle does not view information in the same manner as a *value chain*. This model allows planners to view information as a resource and compare it to the other resources of the enterprise, whereas the value chain focuses primarily on the activities and how they provide value.

INFORMATION QUALITY VALUE CHAINS FOR ENVIRONMENTAL INFORMATION

In applying this concept to environmental measurements, we need to identify the key activities that will form the link and place them in their appropriate order. In general, information activities can be divided into *production* and *distribution*. Another model is to divide information quality into the areas of *content* and *delivery.*

A review of processes indicates that one of the biggest activities related to information is the development and maintenance of large databases. Also, prior to the production of any data, the first activity might be the design of the data structure. Simple models, such as the previous suggestion of dividing information into production and distribution, may not provide the activities needed to understand a value chain. The following proposed value chain is for the planning and collecting of environmental samples, analysis, movement into a data system, and subsequent availability for public use.

The table below presents a proposed “group” for each kind of activity, a specific “activity” (link) in the chain, and some suggested associated quality characteristics.

TABLE 1. Environmental measurements information quality value chain

ACTIVITY (LINK)	QUALITY CHARACTERISTIC
design of scientific activity	data quality objectives
	stakeholder input and support
environmental measurements	measurement precision
	measurement accuracy
	measurement representative
	measurement completeness
	measurement comparability
data standard development	representativeness of the data standard
	completeness
	conformance to business rules
	documentation of the data standard
	data name clarity
	data name consistency
environmental sampling activity	conformance to planning document
	completeness of sampling effort
	documentation of field activity
	record correctness
laboratory activity	sample handling/security
	conformance to planning document
	record correctness
	quality controls performed
data collection and input	data entry freedom from defect
	data entry verification process
	data entry validation process
software/operations systems	software validation process
	software verification process
	conformance of software to enterprise requirements

ACTIVITY (LINK)	QUALITY CHARACTERISTIC
	efficiency in software operations
architecture	redundant system processes
	business information model clarity
	operational data model clarity
	distributed database architecture and design
hardware	facility security
	facility conformance to hardware requirements
	hardware conformance to enterprise needs
	reliability of hardware
	hardware maintainability
data warehouse	data architecture relationship correctness
	unnecessary multiple data representativeness
	redundant storage of system data records
	data report potential accessibility
	data report actual accessibility
output/reports/cyber access	data report availability
	data report contextual clarity
	web information availability
	web information accessibility
	page loading speed
	contact information accessibility
	timeliness
	functionality of links
	spelling, clarity, organization
	web site modification timeliness

Using the individual links (activities) identified in the above table, managers and quality

managers can begin to understand not only the processes, but also the value of those processes. Based on this understanding, those quality characteristics that are most valued can be prioritized for consideration for measurement and continued improvement.

For those quality characteristics that are repeated in each value chain link, the quality managers can determine their relationship to the quality characteristic as it might be applied to *information quality*. For example, the following characteristics can be found all across the value chain.

- documentation
- completeness
- correctness
- timeliness

WHAT ARE THE *DATA TYPES* FOR ENVIRONMENTAL INFORMATION?

Because there is not any one single *data type* for the environmental and other information produced or captured and available in USEPA databases, a single *information quality value chain* will not adequately model the quality of all information. To meet that goal, the different *data types* need to be identified. For each *data type* an analysis should be conducted to identify different activities by which data or information can be produced and distributed. Additional value chains may be developed or a more complex value chain may be modeled for each data type to accommodate all the methods by which the data were developed.

Some examples of possible data types include:

- environmental measurement data for a study or single activity
- environmental measurement data from ongoing monitoring
- environmental measurement data provided by third parties
- regulatory environmental measurement data
- other regulatory data (e.g., conformance)
- survey measures
- geospatial data (e.g., GIS)
- modeling data (environmental, financial, demographic, etc.)
- financial data
- demographic
- geographical data
- facility data

Often, work will include more than one data type. For example, data from both GIS and analytical environmental measures can be produced concurrently. Many of the activities (links) can be interrelated. Value chains may not be simply linear; activities may occur on a separate value chain which “feeds” into a specific link on the first value chain. Developing visual models of these value chain relationships may be a useful exercise for quality managers.

SUMMARY

Every manager and quality manager can better understand their role and responsibilities for information quality if they:

- have a model of the entire value chain

- can recognize the activities for which they are responsible
- have knowledge of the information quality from earlier links in the value chain
- have knowledge of the quality expectations for the next link in the chain as well as the end-customers for the information.

The value chain is a useful planning tool to develop a model for information quality.

ACKNOWLEDGMENT

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TECHNIQUES FOR ASSESSING THE QUALITY OF DATA IN DATA WAREHOUSES

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ABSTRACT

Environmental scientists increasingly rely on computer information systems to store large volumes of measurement data in support of individual studies or as an additional data resource. Additional data, collected in the form of "data quality indicators," may also be recorded in these information systems to provide an increased understanding of the value of the measurements data for use in decision-making and science applications. Quality of environmental measurements and any supporting data includes assurance that the data entered into the systems are free of defects.

Quality systems for environmental measurements may need to take into account quality processes to ensure the quality of both the production and distribution of the environmental measurements and supporting data. These quality processes need to include assessment methodologies. This technical paper discusses methodologies to assess the quality of data and information resident in a data warehouse. The areas covered here include:

- identifying appropriate data warehouse quality indicators
- developing assessment procedures
- conducting data warehouse assessment
- reporting data warehouse assessment results
- tracking improvements in data warehouse quality

BACKGROUND

A data warehouse may be created to directly support an individual project with environmental measurements or the warehouse can be created to support a nationwide system of measurements or reports of regulatory data. Data in environmental data warehouses are not always simply environmental measurements and their associated data quality indicator data. Other supporting data can be of interest to customers and workers who use the data.

The quality of the data in the warehouse includes the quality of this supporting data. Sometimes this is referred to as "metadata." A variety of mechanisms can be put in place to help assure the quality of environmental measurements and other data that is resident in a data warehouse.

Data standards

Development of data standards can help ensure the quality of data in a data warehouse. By

providing clear definitions and placing limitations on the type of data that can be entered into a single field in a database, workers can gain an additional assurance of *consistency* in the data. A poorly described data element can be an invitation to "overload" the data, using the data element to record information that could not be easily recorded somewhere else. Standardization, while helping to ensure consistency in data, reduces flexibility; therefore, developers of data standards must be sure to develop robust standards.

Verification and validation processes

As information is collected into a data warehouse system, some workers provide a process to verify and validate *completeness, consistency,* and *correctness* of the data. This process is similar to incoming material inspection at a factory. Product that doesn't pass inspection is returned to the provider to make amends. The same process occurs with verification and validation of software. In the best systems, the provider gets both immediate feedback and some summary of acceptance over time so that the provider can track an improvement progress. Also, the better the supplier gets at providing acceptable data, the less need for a resource commitment to conduct these inspections. Relying solely on inspection to ensure quality is not a good practice. Inspection is best used as a checker and verifier of quality.

Defect correction protocols

Defects may be observed in the data warehouse by external customers as they work with the data. Some systems offer the ability to the external customer to make note of the observed defect and assist in correcting the defect. This is sometimes referred to as an "error correction process." In theory, this process should improve the *correctness* of the data resident in the data warehouse because this is viewed as a quality control process. However, if there are not adequate controls on the defect correction process, the impact of the corrections on the quality of the data may not be assured. Also, without measures of the quality of the data in the data warehouse, the impact will not be known. To make the most use of these protocols, they must be applied in terms of the overall quality system.

The key to understanding and tracking the veracity of all processes that can impact the quality of data in data warehouses is to have a robust information quality system which includes adequate data warehouse assessment processes. The following is a suggested process for implementing assessments of data in data warehouses.

TYPES OF DATA WAREHOUSE ASSESSMENTS

There are many possible ways to construct data warehouse assessments. The following is an overview of assessment types:

Scope

One approach is to consider the product-process-system trilogy:

- **data product** - only data or the data warehouse that is the product of all processes
- **data process** - an individual process (e.g., collection, design, data standards development) related to the data warehouse
- **data system** - entire collection of processes that make up the data warehouse system

Characteristics

Another option is to evaluate data in the data warehouse for one or more individual quality

characteristics. This type of assessment could look at the quality characteristic(s) in one or more processes. For example, in looking at *correctness,* defects could be introduced prior to information collection, during information collection, as data are accessed in the data system and in the reporting of data.

Data element

One option is to only look at specific data elements. An obvious choice would be those of the most interest to the customer, for example, actual values recorded for environmental data measurements.

Assessor source

The source of the assessment can also have an impact on the planning process. For example, the assessment may be internal or it may be external, performed by the quality manager in an enterprise. Alternatively, a customer could also perform an external assessment or vice versa.

WHY CONDUCT A DATA WAREHOUSE QUALITY ASSESSMENT?

An important axiom in conducting assessments is:

> ***Be sure that the purpose of the assessment is known.***

This is important because an enterprise needs to be sure that this is a wise use of enterprise quality resources. Results of an assessment are intended to be an useful tool for improving quality. This can be best assured if the actual purpose and potential use of the assessment results are known. Ensuring the implementation or corrective action and even preventive actions can also be facilitated with good planning. This leads to another good axiom for assessments:

> ***Do not start any assessment process unless the parties involved have already agreed to the process by which corrective actions will be determined and implemented.***

MISCONCEPTIONS ABOUT QUALITY OF DATA IN DATA WAREHOUSES

Some common misconceptions about the quality of data in data warehouses are worth noting:

Misconception 1: The quality of data should be 100% correct.

This misconception fuels the fear of assessments because while many owners of data may hope that their data are of entirely known quality, they know in fact that the data have some degree of defects. Quality experts need to continually remind all customers that very few data systems are free of defects in some form. The best that anyone can do is to try to keep the defects to an acceptable level. This concept is true in all industries. For example in the automotive industry, car manufacturers strive to rid all cars of defects, yet, they continue to experience product failure and in some cases recalls.

Misconception 2: Routine data inspection will ensure 100% data quality *correctness*.

Routine data inspections are quality control processes during the normal course of the data quality life cycle. These inspections provide additional assurance of specific types of data quality; however, the only way to know if inspections work is to perform a statistical analysis of the quality of the data in the resulting data warehouse. Applying quality assurance techniques

allows the enterprise to evaluate the efficacy of the inspection process. This highlights an important quality axiom:

You cannot inspect quality into a product.

This axiom points out the importance of up-front planning so that inspection processes function mainly as verifications of the quality that was planned for in the product.

Misconception 3: 100% inspection and correction will ensure 100% freedom from defects.
Some people believe that if all 1000 items are inspected in a 1000 item database and the five defects found were corrected, then the database is 100% free from defects. A subsequent inspection of all 1000 items might reveal a defect that was not detected in the first inspection. Statistical sampling and analysis of the quality of the data in the data warehouse is the best way to determine and report valid quality measures.

OTHER MISCONCEPTIONS
In addition to the above "quality" misconceptions, misconceptions persist regarding potential usefulness of environmental measurement data related to their value as data in data warehouses.

Misconception 4: Data can be collected so that it is useful to all *secondary users.*
This misconception involves the belief that all environmental measurement data are equal, that they can all be easily expressed in simple terms so that they are comparable and could be potentially used in many possible applications. In fact, environmental measurements are highly complex both in terms of the measurement itself and in terms of the basis of the measurement. The basis of the measurement involves the sample parameters as well as the quality parameters. For example, sampling may have been conducted based on a complex sampling scheme or the samples may be composited in several ways. In order to demonstrate lack of contamination and to verify that a particular laboratory's results are not biased, fractions of samples may be sent to various locations. The order of complexity can make standardization very difficult. However, workers can standardize certain key elements that may increase usefulness of the data for other customers; planning ahead of time for all possible uses is often not reasonable.

Misconception 5: All environmental measurements found in environmental systems are based on scientific and known processes.
In fact, in some cases, gross estimates reported into databases may represent "best guesses." Again, the best approach to do is to provide an indication in the database regarding the quality of the environmental measurement.

Misconception 6: The group in control of a database was responsible or had direct knowledge of the quality inherent in the original environmental measurements.
In fact, many large databases containing environmental measurement data may have data reported into the systems by numerous external parties. Persons responsible for the database may not have had the opportunity to witness or participate in processes that produced the data. Furthermore, they also may have no knowledge regarding the quality system or the implementation of a quality system when environmental measurements were made.

DISTINGUISHING BETWEEN INFORMATION *CONTENT, PRODUCTION AND DISTRIBUTION* QUALITY

USEPA and other groups working with environmental data measurements need to distinguish between those aspects of quality that are related to measurement aspects of scientific data collections process and those related to "delivery" or "processing" of scientific data.

In addition to data about an environmental measurement (such as the value, parameter of interest, units, etc.), often other data are collected that provide value to the environmental measurements. These data are termed "data quality indicators" and are called by some people "metadata." (Metadata are data about data.) Often when individuals working in science applications discuss data quality, they are talking about the quality of the environmental measurement. They are talking about the ***environmental measurement quality***. One approach that might be useful is to delineate the data and "metadata" into various types for purposes of planning assessments of data in data warehouses. For example, for environmental measurements:

DATA TYPE	DESCRIPTION	Example data elements
primary business data	those data that are of primary interest to the customers and workers	parameter value units
data quality indicator data	the data attached to measurement data which give the data value for its use in science applications	precision accuracy representativeness completeness comparability method sensitivity
secondary business data	those data that are of secondary interest to the customers and workers	matrix time GIS and location description facility
computer metadata	those data that are needed for the computer system to operate	field length field type data standard

DETERMINING WHICH ASSESSMENTS OF DATA CAN PROVIDE VALUE

Based on the above discussion, an individual planning assessments can recognize the need to determine which data types are the most critical for an evaluation. With regards to the "content" element of environmental measurements data quality, simply having access to the data quality indicators might be the most important aspect of data quality. Second, and also very important, is knowledge that the data quality indicators as recorded in the data system are as free of defects as possible. Third, assessment of data quality indicators will demonstrate that data are useful for the purpose for which a worker may need them. This third

level is a scientific determination and is not the focus of this technical paper.

ASSESSMENTS

The following sections cover specific areas of conducting assessments of data quality in data warehouses. They consist of pre-assessment planning, working papers, assessment and corrective action implementation.

PRE-ASSESSMENT PLANNING

Pre-assessment planning is the key to successful assessment. Determine where the assessment will be conducted. Can the assessment be performed in your own office or will you need to be on location? The following items should be addressed.

Determine purpose and scope of the assessment

Meet with customer or management representatives and determine assessment purpose and scope. As discussed above, how assessment results may be used is critical in planning the assessment. Collecting assessment information that has no use is a waste of resources. For a database assessment, assessment scope is based on:

- amount of data in the system
- quality indicators that are of interest to the customer

Assessment results often need to be the subject of corrective actions and planning for future preventative actions. If that is the case, the process by which the assessor identifies nonconformances and defects and how the corrective action process will be implemented must be discussed in advance. Assessors may be involved in follow-up review of a written corrective action plan or even the revised information/data product itself. It is critical to establish this process prior to conducting the assessment.

Identify applicable information quality indicators

Meet with the customers for the assessments and determine those information quality indicators that are of greatest interest. Attachment 1 identifies some potential information quality indicators for all aspects of information quality, including data warehouse quality. Some suggested information quality indicators for an assessment include:

- *completeness* (absence of blank data items)
- *unnecessary duplicate records*
- *correctness* (verification to fact, verification to information collected as an intermediary; for example, a field collection data sheet is an intermediary)

Establish measurement methodology

Once quality indicators are selected, the measure of the quality indicator must be determined. There may be more that one possible measure for a single quality indicator. A good example of this is in the case of *timeliness,* which is expressed as two forms of *information float:*

- *information float 1* - the time it takes for an item of information to be collected into a data system from the time information was first available
- *information float 2* - the time it takes for an item of information to be available to a system user from the time it is first collected into the data system

For either type of information float, there are at least two possible measures:

- **time units** - a direct measure of time (e.g., days, hours, minutes, seconds)
- **conformance** - a measure if the information was received in time for its use (e.g., yes or no)

For the three information quality characteristics selected in the previous section, the following measurements are proposed:

information quality characteristic	**measures**
completeness	for each data element, total complete data records in ratio to the total number of data records as a percentage
unnecessary duplicate records	for each data element, total duplicate record in ratio to the total number of data records as a percentage (also may include identification of different types of duplicates as identified during the assessment)
correctness	for each data element, total number of incorrect records in ratio to the total number of data records as a percentage (does not include unnecessary duplicates or incomplete records in the total count of correctness)

Statistical sampling

Selecting a sample of the overall data population may be necessary to evaluate an individual quality indicator. Sampling methodologies include (English, 1999):

- **random sampling** - use of random number generator to provide equal chance to select every item of data
- **systematic sampling** - selection of every n^{th} record, based on ratio of required sample size to total population (for use when data records are already random)
- **stratified sampling** - when there is more than one stratum in the records, to ensure the selection of adequate records in each strata
- **cluster sampling** - selection of subsamples from logical clusters in the database and combining them

Determine the need for acceptability criteria

Depending on the scope of the assessment and maturity of the quality system in place for information and data, the assessor may need to establish acceptability criteria to report any measurement as a nonconformance.

When sample methodology is employed, acceptability criteria form the basis for the determination of sample size based on the desired confidence level. Larry English provides a detailed explanation of the applicability of acceptance sampling methodology in his recent book (English, 1999).

Identify alternative information source

For some quality indicators (e.g., **accuracy to original data**), assessment of information quality may require identification of an alternative or additional information source to use as the basis for comparison. Identify those sources prior to the assessment, if possible, and verify with the customer for the assessment the authenticity/acceptability of the alternative information source.

ASSESSMENT WORKING PAPERS

Develop documents to serve as the basis of the assessment and facilitate recording of both observations and conclusions. This approach is consistent with all assessments. Assessors call these documents "working papers."

Assessment plan

The assessment plan need not be long, but it should be documented and should include:

- assessment identifier (number)
- type of assessment
- scope of assessment
- purpose of assessment
- proposed assessment data
- proposed assessors (phone/address)
- location of assessment
- selected assessment target areas
- contact persons

Assessment standard operating procedures (SOPs)

Develop standard operating procedures for the purpose of conducting routine and consistent assessments and provide training on the SOPs. Include in the SOPs some details of measurement methodology for information quality.

Assessment requirements

Develop a list of assessment requirements based on assessor's expertise and the customer's needs for the assessment. This list of assessment requirements helps focus assessment planning, checklist development and assessment conduct.

Assessment checklist

Develop an assessment checklist to serve as a reminder of all areas that the assessors intend to cover in their assessment of the database. This checklist then becomes a formal record of the assessment in combination with whatever electronic records are created in the process.

Notification and request for information letter/memorandum

Prior to the conduct of the assessment, assessors should formally provide notification of the assessment in a letter or memorandum to the party being assessed. The letter should include the assessment plan. One option is to include the assessment checklist to allow the persons responsible for the data an opportunity to prepare for the assessment.

Reporting format

Provide assessors with a standard reporting format for communicating the results of the

assessment. The structure of this reporting format should reflect the planning for the corrective action process. The most important feature of the report is to ensure that assessors can easily develop this report so that no time is lost in reporting the assessment. The later that assessment results are provided, the less impact and credibility of the assessment process. One method to ensure rapid reporting is to limit the approval process. A well-organized assessment system should empower the assessor to produce a final report with no assessor management review.

ASSESSMENT

Communication during the assessment process is crucial in garnering support during the process and in effective utilization of assessment results.

Pre-assessment briefing

Meet with the parties that are responsible for the database, go over the audit plan carefully explaining the purpose, scope and assessment methodology, and ask if there are any questions. This is a good time to work out last minute details, such as concerns about access to data and how assessment results might be received. Be sure to go over in detail any corrective action processes that were planned.

Assessment implementation

Make a record of all electronic processes used in the assessment process and, if possible, provide a printout and electronic file of any nonconformances identified in the information under review.

Assessment debriefing

At the conclusion of the assessment, be sure to provide the persons responsible for the data and information with a personal debriefing of the findings of the assessment. Discussion of the corrective actions as well as preventative actions that can be implemented immediately may be helpful.

CORRECTIVE ACTION IMPLEMENTATION

Planning actions to correct identified problems with information quality can be a meaningless exercise and a waste of resources unless there is a process to ensure implementation of the planning. Verification by assessors is useful; however, this approach places the burden of verification on the assessors and requires additional resources to perform the verification. The corrective action process should be a standard process of the enterprise that is assessed, and the process must provide some form of verification for each type of finding reported in an assessment.

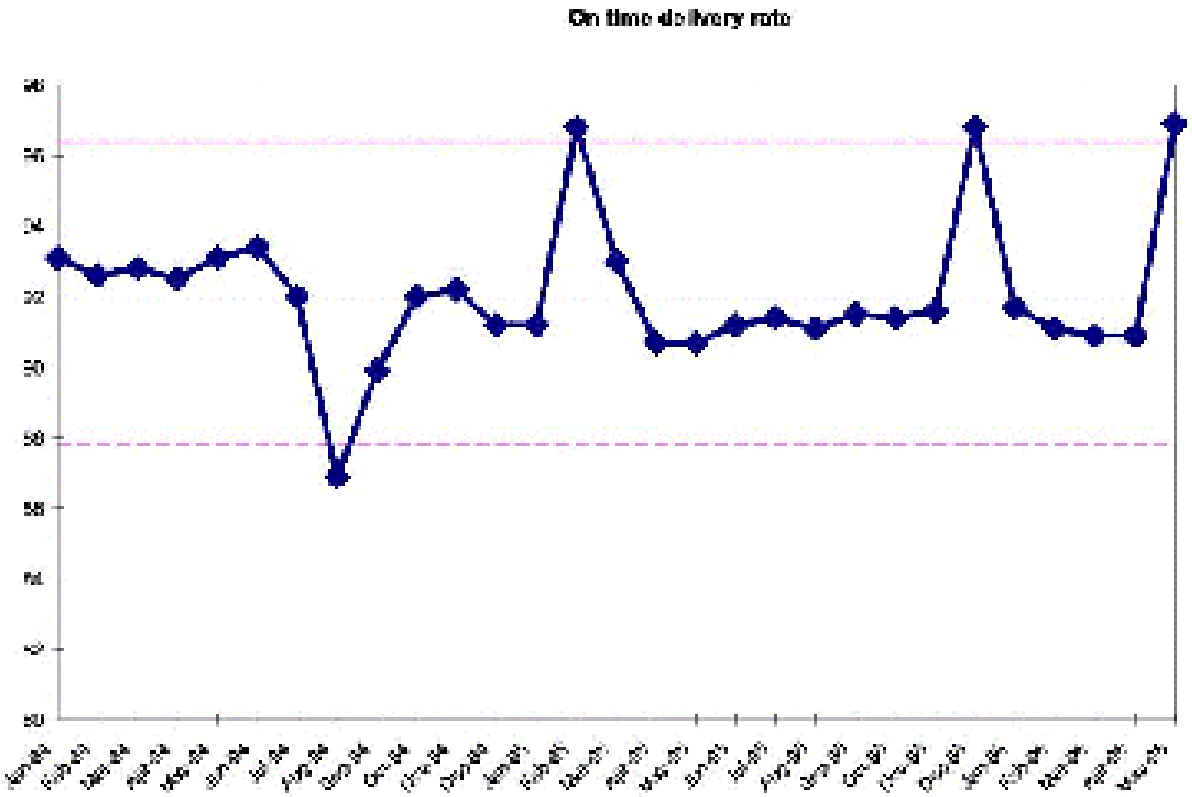
Preventative actions

Establishing preventative action processes will ensure improvement in the quality of the information and reduce reliance on the assessment process to determine and monitor the quality of the information.

ASSESSMENT RESULTS IN ONGOING QUALITY SYSTEM MONITORING

An important use of the results of information quality assessments is for ongoing monitoring operations. For certain information quality indicators, quality managers can routinely monitor

the quality of the information in the form of a **control chart**. For example, the number of defects in information received from an outside party may be a variable subject to measure. Ongoing measurement and charting of the number of defects will allow the quality manager to calculate upper and lower control limits. Using this information, the quality manager can examine the process used to develop the information that is being assessed and determine if improvements to the process actually result in increased quality.



COMMENTS ON MEASUREMENTS

Users of technical information resident in computer systems need to pay special attention to the issue of measuring data quality because the technical information in many cases consists of measurement data. Measurement data includes quality indicators which provide useful information regarding the measurement in terms of the accuracy, bias (precision), representativeness, completeness, comparability and sensitivity of measurement methodology used.

Both technical measurement results and associated quality indicators are quality concerns for information *distribution* because once recorded in the electronic environment, they are essentially equivalent data elements. Assessment of information quality for *distribution* processes is also a measurement process. Development of measurement methodology, acceptance criteria, sampling techniques and confidence intervals results in similar quality indicators for information *distribution.* For example, accuracy and precision of a measurement process to determine the number of defects in a database are important indicators of the

efficacy of the quality measurement.

Assessors must be able to clearly explain the unique nature of the categorization of various types of measurement quality indicators so they can communicate quality system needs, assessment results and opportunities for improvement without confusion.

SUMMARY

Quality managers can apply existing assessment methodologies to all quality aspects of technical information held as data in information systems. A well operated and consistent assessment process will provide valuable tools for managers to know and improve the quality of their information. Identifying usable quality indicators, measures for those quality indicators and acceptance criteria are important processes for planning assessment. Establishing and communicating the relationships of these indicators to specific processes for both production and distribution of information will facilitate development of quality improvement approaches.

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http://www.thedecalogue.com/chartq2.htm - control chart graphic

INFORMATION QUALITY INDICATORS FEATURES MATRIX

TYPE	QUALITY FEATURE	QUALITY INDICATOR	DEFINITION	MEASURE
DATA	data representation	data representativeness	a measure of the degree to which the set of rules for recording data meet the needs of the user	% or Y/N
		data rep. completeness	a measure of the degree to which the set of rules for recording data ensure data are completely represented	% or Y/N
		data rep. documented	a determination if adequate documentation of the data representation is provided	% or Y/N
		data rep. granularity	a measure of the degree to which the rules for recording the data provide for recording the correct amount of granularity	% or Y/N
		data rep. validity to business rule	a measure of the degree to which the rules for recording the data are a valid representation of the associated business rules	% or Y/N
		data name	the degree to which the data name, entity name, attribute name clearly communicate the meaning of the objects named (English, 1999)	% or Y/N
		data name consistency	the degree to which the data and entity names are consistent across all presentation media, such as field names, screens, reports	% or Y/N
	data record	data record accuracy to surrogate	a measure of the agreement of the data record with the information record on a surrogate (such as a field sheet or survey form)	% or Y/N
		data record accuracy to reality	a measure of the agreement of the data record with the data source	% or Y/N
		data record business rule conformance	a measures of the conformance of data values to its domain and business rules	% or Y/N
		data record timeliness (information float 1a)	a measure of time for the data record to be made and for the data record to be placed in a formal data base system	time (days, hours, minutes, etc.)
		data record timeliness (information float 1b)	the measure of failures to accomplish the enterprise's goal(s) because the data record was not available to the data system when needed	failure rate
	data standard	data standards	the degree to which the data standards enable people to easily define data completely, consistently, accurately and understandably	Y/N
INFORMATION CONTENT	scientific measures	measurement precision (meas. accuracy 1)	a measure of mutual agreement among individual measurements of the same property (usually under prescribed similar conditions)	standard deviation
		measurement bias (meas. accuracy 2)	a systematic or persistent distortion of a measurement process which causes errors in one direction (i.e., the expected measurement is different than the sample's true value)	numerical difference between expected and true value
		measurement representativeness	a measure of the degree to which results (data) accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition or an environmental condition (ANSI/ASQC E4-1994)	
		measurement completeness	a measure of the amount of valid results (data) obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions (ANSI/ASQC E4-1994)	
		measurement comparability	a measure of the confidence with which one set of environmental measurement results (a data set) can be compared to another (ANSI/ASQC E4-1994)	
		measurement reproducibility	a measure of the reproducibility of a measurement methodology	

		measurement verification	a measure of the verification that a measurement was assessed to process requirements	
		measurement validation	a measure of the validation of a measurement to results requirements	
		measurement usability	an assessment of a measurement for conformance to use requirements	
		measurement documentation	measurement was adequately documented	
	geospatial measures	to be determined		
		to be determined		
		NOTE: May include quality indicators for scientific measures above.		
	survey measures	to be determined		
		to be determined		
		NOTE: May include quality indicators for scientific measures above.		
	administrative data	conformance to the enterprise's business rule	the degree to which the data conform to all the business rules and administrative requirement of the organization	% or Y/N
	financial data	correct classification	financial data are recorded in the correct classification	% or Y/N
	system meta-data	system meta-data completeness	the degree to which meta-data are complete	%
		system meta-data business rule conformance	a measure of the conformance of meta-data to the business rules	% or Y/N
INFORMATION DELIVERY	data collection and input	data entry freedom from defect	a measure of the correctness in the data entry of information	%
		data verification	the degree to which data were verified to meet process requirements	%
		data validation	the degree to which data were validated to meet output requirements	%
	operations, analysis, software	verification of software	a measure of the degree to which software are verified	% or Y/N
		validation of software	a measure of the degree to which software are validated	% or Y/N
		conformance of software to enterprise requirements	a measure of the degree to which software conform to the requirements of the enterprise	% or Y/N
		efficiency in software operations	a measure of the use of resources compared to the scope and complexity of the assignment	% or Y/N

	architecture *architecture conformance to enterprise information requirements*	redundant system processes	a measure of the redundancy of unnecessary system processes	%
		business information model clarity	a measure of the clarity of the business information model (does it provide all the information needed in a clear manner) (English, 1999)	Y/N
		operational data model clarity	a measure of the clarity of the operations data model (stable, flexible, clear, complete)	Y/N
		distributed database architecture and design	the degree to which the processes control the physical distribution of database data	Y/N
	facility, hardware	facility security		
		facility conformance to hardware requirements	a measure of conformance of the facility to hardware requirements (and enterprise requirements)	Y/N
		hardware conformance to enterprise needs	a measure of the conformance of hardware to enterprise requirements	Y/N
		reliability of hardware	a measure of the reliability of the hardware	failure rate, etc.
		hardware maintainability	a measure of the resources needed to maintain hardware	money or resources
	output/reports (data warehouse)	data report availability	a measure of the availability of reports on data from a data system	% or Y/N
		data report contextual clarity	a measure of the degree to which data presentation enables the information customer to understand the meaning of the data and avoid misinterpretation (English, 1999)	%
	Internet/cyber	web information availability	a measure of the availability of information that is needed by the information customer (see GOAL 7)	% or Y/N
		web information accessibility	a measure of accessibility of information that is needed by the information customer (see GOAL 7)	% or Y/N
		page loading speed	the time it takes for individual pages to fully load at a "normal" work station (Tamini, 2000)	time
		contact information visibility	the presence/absence of contact points if the information customer needs additional information or has a question (Tamini, 2000)	% or Y/N
		timeliness	the amount of time from when information (e.g., environmental data) is available to an organization until it is available to information customers who use the information at the web site (Tamini, 2000)	time
		functionality of links	a measure of the degree to which there are inactive links in a web site (Tamini, 2000)	% or Y/N
		spelling, clarity, organization	a measure of the "readability" of the information provided at a web site	Y/N (potentially subjective)
		web site modification timeliness	the amount of time from when changes need to be made to reflect organization changes (e.g., re-organization, changes in programs, etc.) and the time the changes are made to the web pages. This is the amount of time; incorrect information is being provided to information customers	time
DATA WAREHOUSE	data architecture	data relationship correctness	the degree to which relationships among the real-world objects is correctly represented by the data - *entity type* to *entity type* - *attribute* to *entity type* - *entity type* to *entity subtype*	**% or Y/N**

	storage	duplicate database records	a measure of the number of incidents of duplicate data entry in a single database	**%**
		unnecessary multiple data representation	a measure of the number of incidents where data are unnecessarily entered in more that one data representation	**%**
		redundant storage of system data records	a measure of the agreement of data when data are necessarily entered into redundant storage	
		data report potential accessibility	the degree to which all potential data needed by the enterprise for information customers are accessible (English, 1999)	**%**
		data report actual accessibility	the degree to which the data that are accessible to information customers can be actually accessed (i.e., ease of use) (English, 1999)	**%**
	archiving	archival timeliness	the degree to which data are placed in archival according to enterprise requirements	time or %
INFORMATION COSTS	process failure costs	irrecoverable costs	costs which are not subject to recovery (such as mailing notification letters to the wrong person) (English, 1999)	
		liability and exposure costs	actual costs and potential risks (such as the liability potential if incorrect information is used to make a decision) (English, 1999)	
		recovery costs of unhappy users	the compensation costs and resource costs to fix a problem because of poor information quality (English, 1999)	
	information scrap and rework	redundant data handling and support costs	the costs of developing and maintaining alternative data systems to handle the same data because the information customer cannot use the data in the first database system (English, 1999)	
		costs of hunting or chasing missing information	the costs of finding missing information, lost productivity because those resources were searching for information and the cost of doing “rework” correcting the problem (English, 1999)	
		business rework costs	the costs of re-performing processes that failed, such as reprinting reports because the first report generation efforts failed (English, 1999)	
		workaround costs and decreased productivity	the costs of performing alternative work, when poor quality information prevents performing the normal process, such as completing administrative documents manually when the software fails to work (English, 1999)	
		data verification costs	the costs to the information customers of performing additional manual “quality inspections” to verify the quality of the information because they do not trust the quality (English, 1999)	
		software rewrite costs	the costs to fix application programs when they fail, recover from the problems caused and rerun the programs (English, 1999)	
		data cleansing and correction costs	the costs of data cleansing (which are usually waste costs because they would often be unnecessary if the information was correctly created and maintained)	
		data cleansing costs	the costs of software to cleanse data from a source database (English, 1999)	

STATUS OF RCRA ORGANIC METHODS PROGRAM

B. Lesnik
U.S. EPA

Abstract not available.

APPLICATION OF SOLID PHASE EXTRACTION AND RAPID LARGE VOLUME INJECTION FOR ROUTINE ANALYSIS OF ENVIRONMENTAL SAMPLES VIA USEPA SW846 METHOD 8270D

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Abstract

Utilizing EPA's Performance Based Measurement System (PBMS), environmental laboratories can readily incorporate new technology into the routine analysis of environmental samples. Under this program, Eastman Chemical Company's environmental laboratory has used automated solid phase extraction and rapid large volume injection to eliminate the post-extraction concentration step normally required for analyses of semi-volatile compounds in environmental aqueous matrices. Solid phase extraction data is compared to liquid/liquid extraction data for wastewater, surface water, groundwater and clean matrices. Data on two solid phase absorbents, divinylbenzene (DVB) and C-18 for the various aqueous environmental matrices are presented. The data obtained show that solid phase extraction yields a higher percent recovery on typical semi-volatile compounds in "real-world" matrix samples than does the traditional liquid/liquid extraction techniques. C-18 sorbent yields higher percent recoveries for nonpolar compounds while divinylbenzene yields higher percent recoveries for slightly polar to polar compounds

Introduction

Traditionally, liquid/liquid extraction techniques have been used in environmental laboratories to remove semi-volatile compounds from aqueous matrices. A one liter sample is extracted multiple times with methylene chloride resulting in ~200 mL of extract. The dilute sample extract must be reconcentrated by (Kuderna-Danish) or nitrogen purge evaporation of the solvent in order to achieve the desired detection limits. Extraction and reconcentration are time-consuming steps that contribute significantly to the poor precision and accuracy often observed in the analyses of semi-volatile compounds. The elimination of these steps has been reported[1] using solid phase extraction and temperature programmable (PTV) injectors. However, these applications are not widely utilized by environmental laboratories. With current technology, it is possible to eliminate the post-extraction concentration step for analyses of semi-volatile compounds for environmental samples without sacrificing detection limits. The implementation of these technologies dramatically reduces the labor requirements to process samples, reduces solvent usage and improves turn-around-time from days to hours. Improved percent recovery of analytes and better precision are also achieved.

The prescriptive methodology of environmental regulations has impeded the introduction of new technology in environmental laboratories. However, EPA's Office of Solid Waste has shown much greater flexibility in use of new methods. Under PBMS, any method that yields acceptable data quality for the particular application may be used. Published methods may be modified, as necessary, to generate acceptable data without pre-approval by EPA. New technology may be used as soon as it is developed and validated, provided that it can be

demonstrated to be appropriate for generating acceptable data quality for a particular application. However, it is the responsibility of the user to show that the method will generate acceptable data quality to meet the data quality objectives (DQOs) for the environmental project. The application of PBMS is applicable to many of the environmental programs that fall under the Resource Conservation Recovery Act (RCRA). Thus, to use the techniques of automated solid phase extraction and rapid large volume injection for routine analysis of RCRA type samples, one only needs to demonstrate the applicability of the method for the specified matrix or project of interest.

Typical aqueous environmental matrixes were evaluated using traditional liquid/liquid extraction techniques and automated solid phase extraction and rapid large volume injection. The performance data obtained are used to show the applicability of automated solid phase extraction and rapid large volume injection to the routine analyses of environmental samples for semi-volatile compounds.

Experimental

Standards:

Surrogate: C-371 BNA Surrogates, NSI Solutions, Inc., P.O. Box 12313, Research Triangle Park, NC 27709

MDL mix: Q-1419 Custom Spiking Mix (NSI Solutions, Inc.)

Methylene Chloride	Burdick & Jackson GC/GC-MS	BJGC299-4
Sodium Sulfate	J. T. Baker	JT3375-5
Methanol	J. T. Baker (HPLC Grade)	JT9093-3
Acetone	J. T. Baker (HPLC Grade)	JT9002-3
HCl	Fisher Trace Metal Grade	A508-212

Equipment

Horizon Technology Inc. SPE - DEX® Automated Extraction System
ATAS OPTIC2 Programmable Temperature Vaporization (PTV) injector
HP6890 GC equipped with HP7683 ALS
HP 5973 MSD
30meter Restek Rtx-5 capillary column with 0.25mm ID and 0.50 µm film
ATAS packed liner (part # A100095) containing a proprietary packing material (Available from Scientific Instruments Sales and Service, LLC Roundrock, TX)
J. T. Baker Speedisk™ # 8067-06, DVB, Auto
J. T. Baker Speedisk™ # 8062-06, C-18, Auto

Extraction Procedure

Horizon Technology Inc. SPE - DEX® Automated Extraction System is used to perform the solid phase extraction on typical environmental matrix water samples such as wastewater, groundwater and surface water. The method is based on EPA method SW846 3535A. The samples are delivered to the laboratory in 500ml bottles. The surrogate compounds used to monitor method performance are added to each sample, then the pH of the samples are adjusted to <2 with HCl. Specially designed caps from Horizon Technology are screwed onto the sample containers such that they can be placed directly onto the SPE-DEX extractor. After inserting an extraction disk and placing the sample container into the extractor, the extraction process is initiated by execution of a pre-programmed method. All steps of the extraction

process (purge, prewetting, sample delivery, solvent delivery and rinse) are automated via a programmable SPE-DEX controller. The extraction disk (J. T. Baker Speed Disk C-18 or DVB) is placed in the automated extractor. The extract (12 to 15 mls) is collected in a sample collection vial placed below the extraction disk. After drying with anhydrous sodium sulfate, the sample is diluted to 30 mLs with methylene chloride ($MeCl_2$) for GC/MS analysis. One ml of extract and the internal standards are added to a GC injection vial. The vial is then sealed with a crimp cap.

Comparative liquid/liquid extractions of base-neutral compounds were performed using EPA method SW846 3510C. Only base-neutral compounds were extracted. A one liter aqueous sample was adjusted to a pH > 11 and extracted three times with methylene chloride. The resulting extract was dried with anhydrous Na_2SO_4 and concentrated before performing GC/MS analysis using EPA method SW846 8270. The extract was concentrated to 30 mL when large volume injection was used. The extract was concentrated to 1 mL when standard injection techniques were used.

Solid Phase Extraction Disk

The extraction disks were obtained from J. T. Baker. The BAKERBOND Speedisk™ resists clogging and exhibit high throughput rates even when samples contain suspended solids. The Speedisk™ are available with a number of sorbents. The sorbents, Divinylbenzene (DVB) and C-18 modified silica gel, were used to extract semi-volatile compounds from aqueous matrices. The BAKERBOND Speedisk™ DVB sorbent is composed of 150 Å, 10µ spherical divinylbenzene. The DVB disk is recommended for extraction of polar compounds. The Speedisk™ C-18 sorbent is chemically modified 60 Å, 10µ irregular silica. The C-18 disk is recommended for extraction of nonpolar to slightly polar compounds.

Temperature Programmable Injector (PTV)

The ATAS OPTIC 2 (PTV) injector was used for injection of the extract onto the analytical column. This injector allows for the increase in the injection volume from 1-2 µL for standard injection techniques up to volumes of 100 µL. The specified volume of extracted sample, 40 µL for the studies in this paper, is injected via the auto injector onto the packed liner (ATAS part # A100095). The injector is operated in the splitless injection mode with solvent elimination. The temperature of the injector is maintained at 10 ºC during the solvent elimination mode using liquid CO_2. During this phase, the extraction solvent (methylene chloride) is eliminated without volatilizing the compounds of interest. After solvent elimination, the split vent is closed and the temperature of the injector is rapidly ramped at 8 ºC/sec to a temperature of 305 ºC. The transfer pressure is increased to 25 PSI to insure that the volatilized analyzes are efficiently transferred to the analytical column. This technique, often referred to as rapid large volume injection or rapid at-once injection, makes it possible to inject more highly diluted samples and maintain the same sensitivity.

Chromatographic System

Analyses were performed on an HP6890 GC and HP 5973 MSD equipped with an HP7683 ALS. The chromatographic separation was performed on a 30 meter Restek Rtx-5 capillary column with 0.25mm ID and 0.50 um film operating at 40-135 ºC @ 20 ºC/min, IH=3 min, then 135-320 ºC @ 10 ºC/min. Pressure pulse and electronic carrier pressure programming were controlled via ATAS OPTIC2 controller unit.

Performance data was established for characteristic aqueous environmental matrices (wastewater, groundwater, surface water and a reagent water) by spiking these matrices with semi-volatile compounds and determining percent recovery through the extraction and analysis processes. Spiked reagent water (clean matrix) is identified as a laboratory control sample (LCS). The determinative method for the analysis is EPA method SW846 8270 (a GC/MS analysis method).

Results

Clean Matrix (Laboratory Control Sample)

For comparison of liquid/liquid extraction and automated solid phase extraction, reagent water was spiked with the MDL mix. This mix contains 65 semi-volatile compounds that are often analyzed under RCRA projects using method SW846 8270. Not all compounds in the mix were analyzed as the GC/MS was calibrated for a limited number of compounds. The performance of liquid/liquid extraction of base-neutral semi-volatile compounds was compared to solid phase extraction using C-18 and DVB disk by spiking reagent water at 100 ppb. Phenolic compounds were spiked at 200 ppb. The results of the study are shown in Table 1 below.

Table 1. Comparison of LLE with SPE in a Clean Matrix (LCS)

Sample	LCS	LCS	LCS
Extraction Process	DVB	C-18	LLE
Compounds	% Recovery	% Recovery	% Recovery
Phenol	23	11	N/A
2-Chlorophenol	62	19	N/A
1,4-Dichlorobenzene	56	65	69
Benzyl Alcohol	32	12	
o-Cresol	62	21	N/A
m,*p*-Cresols	63	20	N/A
N-Nitroso-di-*n*-propylamine	72	76	80
1,2,4-Trichlorobenzene	62	73	69
Naphthalene	63	81	67
2-Methylnaphthalene	68	95	72
1,4-Naphthoquinone	76	-	-
Acenaphthylene	68	84	69
Acenaphthene	71	84	71
2,4-Dinitrophenol	62	50	N/A
2,4-Dinitrotoluene	83	72	82
4-Nitrophenol	61	28	N/A

Table 1. Comparison of LLE with SPE in a Clean Matrix (LCS) (continued)

Sample	LCS	LCS	LCS
Extraction Process	DVB	C-18	LLE
Compounds	% Recovery	% Recovery	% Recovery
Dimethylphthalate	78	-	78
Diethylphthalate	82	88	80
Fluorene	75	88	67
Phenanthrene	76	86	72
Anthracene	75	84	74
Di-*n*-butylphthalate	81	84	82
Fluoranthene	82	85	75
Pyrene	76	88	82
Butylbenzylphthalate	76	91	87
Benzo[a]anthracene	77	85	76
Chrysene	75	89	80
Bis(2-ethylhexyl)phthalate	77	90	86
Di-*n*-octylphthalate	76	89	-
Benzo[b]fluoranthene	77	95	74
Benzo[k]fluoranthene	77	75	76
Benzo[a]pyrene	71	82	80
Nitrobenzene-d_5 (surrogate)	65	26	71

Solid phase extraction with DVB gives equivalent performance to LLE in a laboratory control sample spiked @ 100 ppb. Solid phase extraction with C-18 disk showed superior performance to LLE and DVB for nonpolar compounds. DVB exhibits superior performance on slightly polar to polar compounds.

Evaluation in wastewater matrix

Effluent from the Eastman Chemical Co. activated sludge treatment system was used to evaluate performance of solid phase extraction in a wastewater matrix. The Eastman facility located in Longview, TX, is a manufacturer of organic chemicals and plastics. The effluent was spiked with the MDL mix at 100 ppb with the exception of phenols which were at 200 ppb. Liquid/liquid extraction and solid phase extraction with DVB and with C-18 were performed on the spiked samples. All samples were analyzed using RLVI. The results of the evaluation are shown in Table 2 below.

Table 2. Comparison of LLE with SPE for Wastewater Matrix

Sample matrix	Wastewater	Wastewater	Wastewater
Extraction Process	DVB Disk	C-18 Disk	LLE
	% Recovery	% Recovery	% Recovery
Phenol	18	12	N/A
2-Chlorophenol	67	16	N/A
1,4-Dichlorobenzene	67	77	49
Benzyl alcohol	12	8	-
o-Cresol	61	16	N/A
m,*p*-Cresols	55	16	N/A
N-Nitroso-di-*n*-propylamine	70	70	50
1,2,4-Trichlorobenzene	74	83	50
Naphthalene	76	86	53
2-Methylnaphthalene	79	92	-
Acenaphthylene	88	86	58
Acenaphthene	83	87	55
2,4-Dinitrophenol	84	67	N/A
2,4-Dinitrotoluene	91	74	55
4-Nitrophenol	N.D.	41	N/A
Dimethylphthalate	81	93	-
Diethylphthalate	84	87	50
Fluorene	80	88	53
Phenanthrene	77	89	52
Anthracene	77	87	49
Di-*n*-butylphthalate	82	86	53
Fluoranthene	82	86	41
Pyrene	73	92	40
Butylbenzylphthalate	83	96	47
Benzo[a]anthracene	80	89	41
Chrysene	78	92	49
Bis(2-ethylhexyl)phthalate	92	92	35
Di-*n*-octylphthalate	78	87	47

Table 2. Comparison of LLE with SPE for Wastewater Matrix (continued)

Sample matrix	Wastewater	Wastewater	Wastewater
Extraction Process	DVB Disk	C-18 Disk	LLE
	% Recovery	% Recovery	% Recovery
Benzo[b]fluoranthene	75	89	39
Benzo[k]fluoranthene	72	77	40
Benzo[a]pyrene	73	81	39
Nitrobenzene-d_5	66	31	55

Solid phase extraction with DVB and C-18 gives superior performance to LLE in wastewater spiked @ 100 ppb. The C-18 sorbent exhibits superior performance to DVB for nonpolar compounds. DVB exhibits superior performance to C-18 for slightly polar and polar compounds.

Evaluation in groundwater matrix

A representative groundwater monitoring well located on the Eastman facility in Longview, TX, was selected for evaluation of solid phase extraction in a groundwater matrix. The groundwater was spiked with the MDL mix at 100 ppb with the exception of phenols which were at 200 ppb. Liquid/liquid extraction, solid phase extraction with DVB and with C-18 was performed on the spiked samples. All samples were analyzed using RLVI. The results of the evaluation are shown in Table 3 below.

Table 3. Comparison of LLE with SPE for Groundwater Matrix

Sample matrix	Groundwell	Groundwell	Groundwell
Extraction Process	DVB	C-18	LLE
	% Recovery	% Recovery	% Recovery
1,4-Dichlorobenzene	47	64	58
N-Nitroso-di-*n*-propylamine	73	69	60
1,2,4-Trichlorobenzene	64	73	60
Naphthalene	68	75	62
Acenaphthylene	74	78	61
Acenaphthene	75	82	61
2,4-Dinitrophenol	115	67	N/A
2,4-Dinitrotoluene	89	73	64
4-Nitrophenol	117	43	N/A
Dimethylphthalate	84	102	-
Diethylphthalate	84	81	64

Table 3. Comparison of LLE with SPE for Groundwater Matrix (continued)

Sample matrix	Groundwell	Groundwell	Groundwell
Extraction Process	DVB	C-18	LLE
	% Recovery	% Recovery	% Recovery
Fluorene	73	87	61
Phenanthrene	65	90	59
Anthracene	60	89	59
Di-*n*-butylphthalate	67	89	61
Fluoranthene	53	90	58
Pyrene	57	91	57
Butylbenzylphthalate	62	96	52
Benzo[a]anthracene	54	90	62
Chrysene	55	91	66
Bis(2-ethylhexyl)phthalate	60	92	29
Di-*n*-octylphthalate	62	89	27
Benzo[b]fluoranthene	56	89	65
Benzo[k]fluoranthene	55	76	60
Benzo[a]pyrene	55	80	60
Nitrobenzene-d_5	74	26	64

Solid phase extraction with DVB and C-18 gives superior performance to LLE in groundwater spiked @ 100 ppb. The C-18 sorbent exhibits superior performance to DVB for nonpolar compounds. DVB exhibits superior performance to C-18 on slightly polar to polar compounds.

Evaluation in surface water matrix

Sabine River water was selected for evaluation of solid phase extraction in representative surface water. This is a sample that is routinely analyzed by the Eastman Chemical Co. Environmental Laboratory. The river water was spiked with the MDL mix at 100 ppb with the exception of phenols which were at 200 ppb. Liquid/liquid extraction, solid phase extraction with DVB and with C-18 were performed on the spiked samples. All samples were analyzed using RLVI. The results of the evaluation are shown in Table 4 below.

Table 4. Comparison of LLE with SPE for a Surface Water Matrix

Sample matrix	Sabine River	Sabine River	Sabine River
Extraction Process	DVB	C-18	LLE
	% Recovery	% Recovery	% Recovery
Phenol	34	12	N/A
2-Chlorophenol	58	24	N/A
1,4-Dichlorobenzene	46	69	56
Benzyl alcohol	26	10	-
o-Cresol	73	23	N/A
m,*p*-Cresols	82	22	N/A
N-Nitroso-di-*n*-propylamine	78	68	56
1,2,4-Trichlorobenzene	54	77	56
Naphthalene	61	79	57
2-Methylnaphthalene	62	102	-
Acenaphthylene	62	80	57
Acenaphthene	63	83	58
2,4-Dinitrophenol	57	68	N/A
2,4-Dinitrotoluene	76	72	57
4-Nitrophenol	65	43	N/A
Dimethylphthalate	74	105	-
Diethylphthalate	76	84	56
Fluorene	67	87	58
Phenanthrene	72	89	59
Anthracene	68	88	57
Di-*n*-butylphthalate	73	87	65
Fluoranthene	66	88	58
Pyrene	63	91	59
Butylbenzylphthalate	79	96	61
Benzo[a]anthracene	72	89	56
Chrysene	73	91	61
Bis(2-ethylhexyl)phthalate	79	92	49
Di-*n*-octylphthalate	75	89	47

Table 4. Comparison of LLE with SPE for a Surface Water Matrix (continued)

Sample matrix	Sabine River	Sabine River	Sabine River
Extraction Process	DVB	C-18	LLE
	% Recovery	% Recovery	% Recovery
Benzo[b]fluoranthene	71	88	53
Benzo[k]fluoranthene	68	74	54
Benzo[a]pyrene	70	80	52
Nitrobenzene-d_5	69	29	59

Solid phase extraction with DVB and C-18 gives superior performance to LLE in surface water spiked @ 100 ppb. The C-18 sorbent exhibits superior performance to DVB for nonpolar compounds. DVB exhibits superior performance to C-18 on slightly polar to polar compounds.

Summary

In the aqueous matrices normally processed by environmental laboratories, automated solid phase extraction exhibits superior performance over the traditional method of liquid/liquid extraction. The divinylbenzene sorbent will extract both polar and nonpolar compounds from aqueous matrices with a reasonably high degree of efficiency. Improved extraction on nonpolar can be achieved by using C-18 sorbent. The implementation of automated solid phase extraction and rapid large volume injection for the routine analysis of environmental samples makes it feasible to eliminate the post-extraction concentration step normally required for semi-volatile compounds by method SW846 8270. By elimination of this labor-intensive step, the following advances are achieved:

- The amount of analyst's time required to process a sample is greatly reduced. Automated solid phase extraction requires approximately 15 minutes of the analyst's time to prep. In contrast, liquid /liquid extraction using method SW846 3510C requires at least 1 analyst hr per sample to process. A four-fold increase in productivity was realized with the use of automated extraction and RLVI. The number of samples extracted by the Eastman Chemical Company Environmental Laboratory increased from 8-12 samples per day to greater than 50 with the use of 4 automated extractors.
- Accuracy and precision are improved by automated solid phase extraction and the elimination of an analytical step. The post extraction concentration step is subject to the introduction of significant error. The more volatile compounds in the extract can be lost with the solvent. Percent recovery on the low boiling point semi-volatile components is often observed to be significantly less than the higher boiling semi-volatile compounds.
- Solvent usage is dramatically reduced. Liquid/liquid extraction requires >200mls of solvent (methylene chloride) per sample. With solid phase extraction this is reduced to approximately 30 mls. This not only reduces initial solvent cost but also reduces solvent disposal cost.
- Turn-around-time on sample analysis can be dramatically improved. It is possible to have a sample completely processed and ready for GC/MS analysis within 30 minutes using automated solid phase extraction. With liquid/liquid extraction, 1-day turn-around

would likely be the best most laboratories would offer.

Under EPA's PBMS program new technology such as automated solid phase extraction and rapid large volume injection can be readily incorporated into the environmental laboratory for routine analysis of samples.

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DEVELOPMENT OF CAPILLARY ELECTROPHORESIS METHOD FOR PHENOXYACID HERBICIDES AND PHENOLS

S. Li

No abstract available.

U. S. ENVIRONMENTAL PROTECTION AGENCY DATA AND INFORMATION QUALITY STRATEGIC PLAN

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ABSTRACT

In July 2000, a Data and Information Quality Strategic Plan Workgroup began analyzing the Environmental Protection Agency's quality system processes to identify where data quality vulnerabilities exist. This paper highlights some of the factors that brought this workgroup together, their analytic process and the six recommendations that resulted, and the current status of this effort.

INTRODUCTION

Data and information are vital to informing public policy decisions and the regulations that help protect the nation's air, land, and water–the mission of the Environmental Protection Agency (EPA). Reliable information and data of documented quality also constitute a valuable resource for the public and leaders across society who increasingly demand access to accurate environmental information that is comparable and complete.

In recent years, the Agency's data and data systems have come under increasing scrutiny from Congress, federal offices including the General Accounting Office (GAO), EPA's Office of Inspector General and Science Advisory Board, and the Office of Management and Budget. These organizations and various groups external to the federal government have asserted the Agency's environmental data lack validity, consistency and reliability. Concerns have been raised regarding the defensibility of the Agency's policy and regulatory decisions that are data-based.

Most of EPA's major data collections were initiated decades ago, prior to the current understanding of data quality principles and in the absence of the standards and metadata requirements that are vital to the reliability and secondary use of data. The vast majority of data used by the Agency is collected by state and local agencies and the regulated community, using inconsistent collection and analytical methodologies, identification standards and documentation. The impact of this variability was noted in a February 2000, GAO report stating that, due to unreliable data, the Agency is unable to give an accounting of the environmental health of the nation's water bodies.[1] The report cited several causal factors, including inconsistencies in water body assessments and methodologies, lack of standards and common definitions, and questionable data consistency and reliability.

EPA's new information office, the Office of Environmental Information (OEI) was established in October 1999. Since that time numerous separate inquiries regarding the state of the Agency's data quality were sent to OEI from Senators Bond, Smith, Baucus, House Committee Chairmen Fowler and McIntosh, and others. EPA's data quality and completeness are squarely on their radar screen and the new office has raised expectations that these issues

will receive greater attention from EPA. In March 2000, Margaret Schneider, Principal Deputy Assistant Administrator for OEI, testified before the House Subcommittee on Oversight, Investigations and Emergency Management, Committee on Transportation and Infrastructure, to answer questions on the "quality" of the Agency's data, and in a follow-up request from the House Subcommittee a data quality assessment was requested for four EPA data systems. The assessment was completed and a report submitted to Congress in August 2000.

DATA AND INFORMATION QUALITY STRATEGIC PLAN

The Quality and Information Council, the Agency's senior management body for deciding information and quality policy, is assisted by four subcommittees. One, the Quality Subcommittee, formed a cross-Agency workgroup in July 2000, to develop a Data Quality Strategic Plan (DQSP). The Subcommittee's charge to the Workgroup was first to identify where and how to improve the quality of the Agency's *environmental* data and second, to recommend how to improve the *quality culture* at EPA; to further embed an appreciation for the role and importance of quality assurance at all levels.

THE PROBLEM OF QUALITY

There are numerous factors involved in even discussing data quality. The very expression is matrix-like in complexity, where the x-axis could represent different *types of data* (regulatory compliance, permitting, violations, ambient concentration measurements, geo-spatial, laboratory analysis, monitoring, technology performance data, etc.) and the y-axis represents different *types of quality* along the entire information life cycle that involves planning, sample measurement, laboratory analysis, data assessment, transmission protocols, database storage and information products. At any given point on this x-y grid, the notion of "quality" takes on different meanings to the different but related disciplines of quality assurance, information management and information technology.

The conventional wisdom among EPA's data detractors and among some EPA staff, appears to be that in general, the Agency's data is unreliable. This view is part perception but is not without an empirical basis. Because standard data quality assessments are not routinely performed on the Agency's data, we lack a baseline, and even standard quality criteria by which to determine the veracity of this conventional view.

For certain data systems which were recently assessed for "quality," the Toxic Release Inventory System and Safe Drinking Water Information System, for instance, the aspect of quality examined is primarily at the *data system* level. The question answered is not, 'do the values accurately represent the actual pollutant release or ambient condition,' but rather, 'are the data in the data repository consistent and complete in comparison to the originating source (a facility reporting form or state data system)?' While this back-end assessment of "quality" is of value, it reports nothing about highly significant front-end stages of the data lifecycle.

EPA's major statutes and the programs they have spawned are dissimilar in purpose and structure. Clean Air Act regulations and guidance are quite specific in their quality assurance requirements for ambient air monitor siting requirements, instrument precision testing protocols and the scientific rigor that underpins the entire monitoring program. The Superfund Program has also developed an effective quality management system and its data and

analysis are generally of known quality. The same cannot be said for all EPA environmental data programs.

A final significant issue is the *source* of most of EPA's data–state and local agencies and the nation's reporting facilities. Congress and the Agency's constituents and customers hold EPA responsible for the data in its systems, regardless of who originally collects the data. Yet, since the majority of its environmental data originates elsewhere, questions are raised regarding how much influence the Agency can exercise over the data collection, measurement protocols and estimation processes which directly impact the precision and accuracy of data.

THE WORKGROUP'S METHODOLOGY

Assessment of Reviews

The Workgroup analyzed reviews of EPA's data and information quality management, by oversight organizations such as the General Accounting Office, Science Advisory Board, National Academy of Public Administration, the Environmental Council of the States and business groups such as the Business Roundtable and Coalition of Effective Environmental Information. A few examples of these critiques follow.

The Science Advisory Board:[2]

1. EPA's Quality System implementation is uneven and varies from organization to organization, increasing the likelihood of problems with data quality;
2. Incomplete implementation of the Agency's Quality System precludes proper evaluation and produces the potential for waste, fraud and abuse;
3. Senior managers need to be champions for successful implementation of the Agency's Quality System and need to implement a more complex web of persuasion, administrative mandates and rewards.

In March 2000, GAO reported that the National Water Quality Inventory, or 305(b) report on surface waters, is not a reliable representation of nationwide water quality conditions due to *incomplete and inconsistent data*, yet EPA uses this report for decision making because it is the only source on whether waters are meeting water quality standards.[3] No factual understanding of how well the Agency is achieving its mission to protect the nation's waters exists.

EPA's Office of Inspector General has identified weaknesses in the Agency's quality system implementation and management, stating, "Without an effective Agency-wide program, EPA could not fulfill its mission" which depends on having environmental data of known and adequate quality.[4]

In the National Academy of Public Administration's November 2000 report, *Transforming Environmental Protection for the 21st Century*, four of ten recommendations apply to EPA's Quality System:

- Invest in Information and Assessment. "Develop objective data of high quality."
- Hold States Accountable For Results. "Redefine EPA's expectations of states in terms of environmental results rather than only process."
- Invest in Information. "Appropriate sufficient funds for major improvements in environmental data."

- Challenge EPA, Congress, and One Another to Transform Environmental Governance. "Build evaluation into the design of . . . programs."

The Business Roundtable (BRT) has developed their *Blueprint 2001*: *Drafting Environmental Policy for the Future*, which includes the following recommendations:

- EPA needs a more a disciplined focus on data quality and scientific rigor.
- Improve data collection, use electronic data collection and reporting, move toward integrated reporting, recordkeeping and monitoring.
- The government should provide better information stewardship, policies that place environmental information in context and tools for assessing its accuracy.

Sherwood Boehlert, chairman of the House Science Committee, has endorsed BRT's proposal to move to performance-based management and has promised the group to take a serious look at these proposals. Boehlert said:
Sound science is the key to reaching consensus on tough environmental problems, and technology is the key to affordably solving those problems.[5]

Analytical Process
Building upon the observations and comments of external reviewers, the Workgroup developed a 12-step data and information lifecycle model to identify *where* along the lifecycle, vulnerabilities to data quality exist, and then identify ways to mitigate those vulnerabilities. The model spanned from planning for a data collection to ultimate storage in a data system. About 90 recommendations resulted from that exercise. The Workgroup next grouped this long list under five categories and developed white papers exploring seven key themes. Finally, interviews were conducted with managers, and data collectors or evaluators from all program offices and six regions–a total of 40 interviews–to better understand the view of decision makers regarding their use of data, quality priorities and expectations of a Data and Information Quality Strategic Plan (DIQSP).

RECOMMENDATIONS
The Workgroup developed seven sets of recommendations and prioritized them according to their importance for improving data quality and quality management. These recommendations were approved by the Quality Subcommittee in March 2001, and presented to the full Quality and Information Council the following May. The list of recommendations appears below, followed by a description of each.

- Create a Chief Information Officer Network
- Require Use of Standardized Quality Indicator Data
- Routinely Report on Data Quality
- Increase Data and Information Quality Training
- Implement Quality Requirements in Grants
- Establish a Model Approach to Information Product Development

RECOMMENDATION #1: Create a Chief Information Officer (CIO) Network
The purpose of the CIO Network is to provide the governance needed for a series of interrelated quality and information responsibilities. The Workgroup and a majority of middle and senior-level managers who were interviewed, identified *senior manager commitment* as critical to improving the *implementation* of EPA's information quality processes. Their view is

consistent with the view of professionals such as quality expert Larry English. From his work in 30 countries, English reports seeing repeated variations on the same theme, "*Management accountability* for information quality is missing."[6]

In some Agency organizations, quality assurance processes (QA) are perceived as an optional overhead expense or an obstacle that may be reduced or eliminated to meet deadlines. Current organizational placement of QA management responsibilities does not necessarily foster management accountability or consistent QA implementation across the Agency. In many organizations, there is no Agency focal point with the responsibility, accountability and authority to require implementation of the quality assurance processes and requirements along the information lifecycle that are vital to producing reliable data. For that reason, the Workgroup believes the *highest priority* recommendation for improving EPA's data quality is the development of a CIO Network. Working with the QIC, the Network would provide the management structure to combine and harmonize lifecycle activities that contribute to the quality of our information.

What is the CIO Network?
The CIO Network, led by the Agency CIO, would include a team consisting of managers from National Program Offices and Regions, with distributed responsibility and accountability for the governance of information processes that include the implementation of the systematic planning process needed for effective data *collection*, and quality protocols which result in dependable and efficient information transfer, storage, use and archiving.

The Network would pull together the separate but interconnected functions of *information management* and *quality assurance* and provide a focal point within organizations to coordinate these responsibilities, assure implementation of Agency requirements, and help settle significant disputes over interpretation of requirements.

Why a Network is Needed
The Network is needed to re-prioritize and elevate the importance of the *information quality functions* that support development of more reliable and defensible data and information–an identified Agency objective. Better *implementation* and integration of quality protocols throughout the lifecycle are pivotal to improvement. Where Agency quality assurance standards and practices are followed, more reliable data result. Where implemented, the guidance and requirements developed by the Quality Staff have helped produce the most defensible and best documented data in the Agency and even the federal government. The attention of *all levels of management* in an organization is needed to assure that data and information are of known and acceptable quality, but by explicitly identifying key managers with information quality responsibilities, the Network will promote better accountability. In support of the CIO Network, a formal cross-Agency team of data stewards or "data gatekeepers" needs to be identified, to monitor data integrity, assume responsibility for individual systems and coordinate data assessments.

Effective information management should include quality assurance functions built horizontally across the information chain, rather than vertically down stove-pipes. Like many other organizations, EPA needs to continue to move from Industrial Age to Information Age processes. The CIO Network is another step in that direction as a vehicle for horizontal

Agency leadership across a number of complementary disciplines that require close coordination. These efforts include traditional quality assurance, IT quality standards, security, software development methods, data standards and information product development.

Under this scenario, better coordination would make it easier to build data systems engineered to meet the needs of the scientist, the analyst and the information technology specialist.

Network Functions

Currently, the Agency CIO reports directly to the Administrator and has "IM [information management] as a primary function."[7] The CIO has overall responsibility for ensuring the quality of information from data collection planning and sampling, to transmission, storage, use and archiving. OEI's Quality Staff supports the CIO and develops policies, guidance and requirements for data collection, analytical techniques and environmental technologies. Quality assurance policies are also needed for other stages of the information lifecycle, including software validation testing, documentation requirements, and data analysis and presentation methodologies. Other organizational units that support the Agency CIO include critical areas of enterprise architecture, policy development, security and IT standards.

The CIO Network will establish clear lines of responsibility and accountability to continue improving the Agency's data and information quality. *Associate CIOs* (ACIOs) will be the *senior quality and information officials* in their National Program Office (NPO) or Region and, with the support of line management in their organizations, will be accountable for implementing directives, standards and procedures that contribute to the quality of data and information in their Office or Region. The ACIOs will report directly to their AA or RA, and to the Agency CIO in matters of quality and information.

The Network formed by the CIO and ACIOs could be used to harmonize approaches to quality assurance, while accounting for the unique features of EPA's regulatory and other programs. It will monitor *implementation* of the Agency's quality assurance planning and process requirements. Network responsibilities are further identified below.

Agency CIO Responsibilities

An array of legislation was passed during the 1990s to help improve the quality and efficiency of information management across the federal sector, including the Clinger-Cohen Act, which created the position of federal *chief information officer*. Federal agencies are still grappling with how to effectively position CIOs to ensure that IM adds value to business and mission performance. According to the GAO, "The CIO position in the federal government is still evolving."[8] The next step in the evolution of EPA's CIO position should be to **explicitly meld the quality program with other CIO responsibilities**, which would include:

- Use of reporting and accountability measures to ensure implementation of quality assurance, information management requirements, June 25, 2001 and standards along the information lifecycle, so that Agency data and information are of known and documented quality.
- Ensuring the use and implementation of approved data standards and metadata

standards for all data collections and in all relevant systems, to help users determine data suitability for primary and secondary uses.

- Establishing criteria and a schedule for *quality assessments* of work along the lifecycle, including field sampling, laboratory audits, transmission protocols, security controls, software validation and including system data.
- Overseeing information quality accountability processes in FMFIA and GPRA, including the NPO and Regional development and progress on annual performance goals and measures for *data quality* for each goal of GPRA under which data are collected.[9]
- Reviewing annual reports from ACIOs that certify the extent to which responsibilities listed above and in EPA requirements are being implemented across the Agency, and identify where further improvements are needed.
- Establishing national quality assurance performance standards and priorities.

Associate CIO Responsibilities

Associate CIOs should be SES-level managers, with information accountability for their region or national program office. The ACIO should be consistently placed across regions and programs in order for the Network to operate as a team of co-equal members for settling information quality issues that transcend a single program or region. Though National Programs and Regions will have some flexibility in designating an ACIO, the Associate CIO must be an SES manager with accountability for the responsibilities listed below. These requirements essentially mirror the Agency CIO responsibilities.

1. Ensure implementation of quality assurance and information management requirements and standards along the information lifecycle, so that Agency data and information are of known and documented quality.
2. Ensure the use and implementation of approved data standards and metadata standards for all data collections and by all relevant systems, to help users determine data suitability for primary and secondary uses.
3. Ensure use of criteria and schedule for *quality assessments* of work along the lifecycle, including field sampling, laboratory audits, transmission protocols, security controls, software validation and system data.
4. Oversee development and progress on annual performance goals and measures for *data quality* for each goal of GPRA under which data are collected.
5. Develop annual reports for the CIO to certify the extent to which quality assurance responsibilities are being implemented across the Agency, and identify where further improvements are needed.
6. Assure implementation of national quality assurance performance standards and priorities.

<u>Quality Staff Responsibilities</u>

The Quality Staff will be responsible for developing and implementing an Agency Information Quality Assessment Program. The Program needs to provide consistent assessment definitions, tools, schedules, criteria for conducting independent audits, a reporting process and other features.

The Quality Staff must help assure that Agency guidance that crosses program and regional boundaries is consistent and appropriate. It needs to seek and respond to input from affected

customers and partners when developing guidance and implementation time-frames and to give consideration to the resources needed to implement guidance–develop a cost estimate of sorts, so that office directors understand the resource commitments that are required to implement new guidance.

The Quality Staff will continue to provide the independence needed for making information quality assessments and identifying corrective actions in Regions and Program Offices, and will advise the Agency CIO and Associate CIOs, to provide the necessary quality assurance expertise they need. Other duties the Quality Staff are currently responsible for would continue.

NPO / Regional Quality Assurance Manager (QAM) Responsibilities
The role of QAMs will be to provide leadership for information quality programs at the operational level in support of the Associate CIO, identifying data quality issues and raising these to line managers and the ACIO. It will be vital that QAMs and the Agency's *senior information resource management officers* communicate regularly to jointly monitor and quality assure, IT resources. The following are included in QAM responsibilities.

1. Support line managers and ACIOs in executing the full range of their information quality responsibilities, including data collection processes, and information management (including IT verification and validation processes), and other duties as described in EPA Order 5360.1.
2. Identify significant information quality needs and issues that require senior management attention and raise these to the appropriate management level.
3. Conduct operations audits to identify needed improvements and monitor compliance with Agency quality requirements.
4. Provide assistance to implement quality assurance standards and requirements.

RECOMMENDATION #2: Require Use of Standardized Quality Indicator Data
Why Are Quality Indicator Data Needed?
Data collection processes are a huge Agency investment. Nearly half of EPA's budget is dedicated to grants and loans, most of which are used to monitor environmental conditions, collect data or build environmental infrastructure. Quality indicator data are needed to obtain data that are of known and defensible quality–to improve the return on data investments by facilitating appropriate primary and secondary uses of data.

Agency data standards are needed for a minimum set of data quality identifiers (e.g., *precision, bias, probability of error*). An Agency policy should formally *require* that these standard data quality identifiers be collected, documented and transmitted as an integral part of all appropriate data collections. In addition, they should be accessible from data repositories, or in the case of legacy systems, be linked to a metadata repository for ease of access. Information products and documents also require supporting metadata to explain the assumptions and methodologies used in data analysis. These metadata could also be stored and maintained in the metadata system.

Where additional metadata are required to meet the particular needs of a National Program Office, the ACIO will be responsible to identify the needed set of metadata and develop

standardized formats for these data. Where possible, the ACIO would ensure program metadata are documented by data collectors (programs, regulated facilities, labs, states and local agencies), transmitted and stored with the data they identify.

The Agency needs to officially identify and use a master metadata repository that contains explanatory information about the data and information products managed by EPA. Such a registry would assist data collectors, system developers and users by providing a single source for obtaining needed metadata and metadata standards for EPA data and products.

Impact on States and Other Data Collectors
This requirement, while vital to improving the reliability and use of environmental data, will need to be developed and implemented with states and others who provide data to the Agency. Cost assessments are needed, along with a plan to phase in metadata requirements. Assistance to data providers will be an important component of successfully implementing this recommendation.

RECOMMENDATION #3: Routinely Report on Data Quality
Why Report on Data Quality?
EPA regularly receives questions from Congress, the GAO, and many other interests regarding the quality of Agency data. Without regular internal assessments, these questions are very difficult to answer. Performing data quality assessments will provide the Agency with a baseline to identify needed improvements and measure progress. As with any major investment and strategic resource, assessment and improvement are key processes for effective management.

Assessment Process
Standardized data quality assessments must be performed on all significant data systems every three to five years (the Agency has guidance on performing these assessments but a more specific *How To* protocol is needed). Associate CIOs will report to the Agency CIO, the results of the data quality assessments in their program or region. With assistance from the Quality Staff, the CIO will determine if a corrective action strategy should be developed to implement improvements. The Agency CIO will, in turn, report on the status of the Agency's data quality to the Deputy Administrator and the Quality Subcommittee.

RECOMMENDATION #4: Increase Data and Information Quality Training
The emphasis on training EPA's workforce has declined in recent years and an array of training is needed. Priority needs identified by the Workgroup involved training for planning and implementing of data collection activities. Training is also needed for statistical analysis, grants management, information product development and training for managers who make data-based decisions. The Quality Staff could assist ACIOs in developing and offering the needed training.

Quality assurance training is vitally needed for field samplers and contract laboratories and training requirements must be included in contract language. Ongoing training should include how to effectively: 1) plan and perform data collection, and 2) assess and audit environmental data. These are the *critical* points at which to assure data *validity,* the degree to which a value actually represents a measured environmental condition.

Grants and contracts management courses that include training on the quality assurance responsibilities of grants/project officers, are very much in need. Grants managers are rewarded for funding grants rather than exercising oversight of the grant requirements such as quality assurance. The use of CD ROMS and Web-based applications and tools could help reduce training delivery costs.

Associate CIOs should identify those in their organizations responsible for various types of data operations, including: sampling, statistical analysis, auditing, etc. These individuals should be *required* to receive appropriate training. Clearly, resources will be needed to provide this training.

RECOMMENDATION #5: Implement Quality Requirements in Grants

Uniform administrative rules have been established for federal grants and cooperative agreements involving non-profits and states. These contain explicit sections on "quality assurance," but the language is not up-to-date and is inadequate to ensure that where environmental data operations exist grantees will establish adequate quality systems. More importantly there is a lack of *implementation* of existing quality planning requirements by grantees, except in cases where a portion of funding is withheld to assure compliance (for instance, by the Office of Air Quality Planning and Standards and certain Regions; the Office of Water recently started a similar program).

Understanding the sensitivity of this issue, the Agency must clarify the quality standards and requirements for states and other grantees collecting data with EPA funds. These standards should be incorporated into grant requirements of delegated programs. Regions and grant administrators should be required to periodically assess recipients' quality systems to ensure that they are implementing quality assurance requirements and are taking corrective action where problems are identified.

At the same time, EPA needs to expand its work with state and local agencies through training and other methods, to build quality assurance capacity for executing systematic data collection and information quality management operations. The Agency Grants Management Manual needs to reinforce the quality assurance requirements for grants and grant managers must receive training on the importance of implementing the quality assurance components of grants.

RECOMMENDATION #6: Establish a Model Approach to Information Product Development

This recommendation addresses the *use* of data and information–the quality of significant information products (IP). A 'significant information product' uses national or regional data to describe environmental conditions, trends and/or the performance of companies, facilities and communities (e.g., the National Air Quality and Emissions Trends Report).

A uniform and comprehensive approach to significant IP development is needed to ensure consistent quality of Agency products. Developers must provide users with the information they need to determine the appropriateness of the product to particular uses, and the degree to which IPs can be linked with other databases and products.

A formal Agency policy should be developed requiring the use of the following five steps as key components to the development of a credible, significant information product. Each office director needs to assume management responsibility for implementing the process described below.

1. Develop an IP plan that incorporates long-term budget needs for development, revisions and performance measurement.
2. During product design and development, conduct a data suitability assessment to ensure that identified data are appropriate for the intended use.
3. Involve the audience and stakeholders during initial development to help clarify objectives.
4. Reference and explain appropriate product-level metadata.
5. Plan to incorporate user feedback, error correction, product updates and methodology revisions.

NEXT STEPS

EPA's Quality and Information Council (QIC) has directed the Workgroup to: 1) identify all the responsibilities for which a CIO Network would be held accountable. And for Recommendations 2 through 6: 2) develop operational steps for implementation, 3) cost estimates and 4) an implementation schedule. To further explore the implications of explicitly melding *quality assurance* and *information management* responsibilities in the Network, the Workgroup is being enlarged to include representatives from disciplines and jurisdictions along the information lifecycle. These include headquarters and regional information resources managers, state data and science specialists, data standards development staff and other areas that were not part of the original Workgroup. Six subgroups have been formed to further develop and refine each recommendation area. This new Workgroup anticipates delivering on its assigned task as described above, to the QIC in September and this analysis will provide the material from which the Data and Information Quality Strategic Plan will be written.

As with any plan, its power to effect change–to improve EPA's environmental data quality over time–will be tied to the degree of its implementation. Because of the existence of the Office of Environmental Information and the responsibility it has been assigned for data quality and information management, the organizational infrastructure now stands ready to support the implementation of the DIQSP recommendations, in whatever final form they take.

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THE INTERGOVERNMENTAL DATA QUALITY TASK FORCE

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ABSTRACT

The consensus mission of the Intergovernmental Data Quality Task Force (IDQTF) is to document an intergovernmental quality system in an effort to address real and perceived inconsistencies or deficiencies with quality systems within and across governmental organizations that result in increased costs, time delays and increased potential risk.

As a first step towards achieving its initial goal of documenting an intergovernmental Quality System, the IDQTF completed the ***Interim Final Uniform Federal Policy for Implementing Environmental Quality Systems*** in November 2000. This policy outlines the requirements for documenting and implementing a quality system and is based on ANSI/ASCQ E-4. The IDQTF also recently completed a draft ***Uniform Federal Policy for Quality Assurance Project Plans*** (UFP-QAPP), which is designed to help Federal departments and agencies use consistent QAPPs that reflect a systematic planning approach to the collection and use of environmental data and technology. The IDQTF is in the process of releasing this draft QAPP Policy for agency review and comment. In addition, the IDQTF is currently developing and refining standardized QA and QC measures used in the Superfund program by the EPA Regions and other Federal agencies. This effort will define minimum QA/QC expectations for Superfund data collection, analysis and review, and reduce the time and effort spent in negotiating QAPP requirements. When complete, these minimum QA/QC measures for Superfund will serve as an appendix to and an implementation tool for the UFP-QAPP.

The IDQTF has initiated the process of developing a framework that outlines the roles and responsibilities of the EPA (headquarters and Regions) and the Federal facilities with regard to QA/QC oversight – another goal of the Task Force.

Implementation of the IDQTF products will be based upon Memoranda of Understanding between EPA and the other partner agencies, DoD and DOE. Implementation requirements will include training on the use of the IDQTF products, which the IDQTF is about to begin developing. In addition to training, the IDQTF is creating implementation tools such as a software program that walks users through the development of QAPPs through the use of linked QAPP worksheets.

ENTERPRISE INFORMATION ARCHITECTURE: IMPROVING INFORMATION QUALITY

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ABSTRACT

Developing a robust information architecture as well as a data architecture helps to ensure the quality of information produced and distributed by an enterprise.

An Enterprise Architecture (EA) is the “explicit description and documentation of the current and desired relationships among business and management processes and information technology. It describes the "current architecture" and "target architecture" to include the rules and standards and systems life cycle information.”[1] An architecture is “the fundamental organization of a system embodied in its components, their relationships to each other and to the environment and the principles guiding its design and evolution.”[2] The EA defines principles and goals and sets direction on such issues as the promotion of interoperability, open systems, public access, end customer or knowledge worker satisfaction and information security.[1]

A quality system is the means by which an organization manages its quality aspects in a systematic, organized manner and provides a framework for planning, implementing and assessing work performed by an organization and for carrying out required quality assurance and quality control activities.[3]

Melissa Cook says in her book Building Enterprise Information Architectures “business leadership for EA development is a must because only the business leaders understand the true information processing needs of the enterprise. It is also a must because it will require executive level understanding and commitment to manage the conflicts that inevitably occur when moving . . . to a controlled and coordinated approach.”[4] The same can be said about quality systems. Quality and business managers can gain much from understanding what an EA is, especially because we need to manage quality for information projects just as we do for environmental data collection projects.

The author reviews enterprise architecture planning, its relationship to quality planning and discusses an example which highlights challenges in applying architecture planning.

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DATA RESOURCE QUALITY FOR LARGE ENTERPRISES[1]

Michael H. Brackett
Data Resource Design & Remodeling

Introduction

Most large public and private sector organizations that have been in existence for several years have large quantities of disparate data and the quantity is growing at an ever-increasing rate. These disparate data cannot be readily integrated to meet the demand for information that supports the business activities in a dynamic organization. This situation puts most organizations in a real dilemma between the rapidly increasing quantities of disparate data and the need to readily integrate those data on short notice to support their business activities.

The only approach to resolving this dilemma is to understand, manage and share all data that are at an organization's disposal within a single, organization-wide, common data architecture. The continued data disparity must be stopped and the existing disparate data must be resolved if an organization is to be fully successful in achieving its business goals. Organizations that do not resolve the dilemma are at risk of not being fully successful at meeting their business goals due to information deprivation.

Business Information Demand

Every organization has a *business information demand* which is the continuously increasing, constantly changing need for current, accurate, integrated information, often on short or very short notice, to support business activities. That demand must be met for an organization to be fully successful at carrying out its business strategies and meeting its business goals. Many organizations are at risk because they cannot readily integrate the rapidly increasing quantities of disparate data to prepare the information necessary to meet their business information demand.

The business information demand is a key part of a six-level *business intelligence value chain*[2]. Value is added from the data resource, up through information, knowledge workers and business intelligence, to support the business strategies and business goals of an organization. The quality of any level in the value chain is no better than the quality of its supporting level. Since the data resource is the foundation level, the quality of support for the business strategies and business goals can be no better than the quality of the data resource.

Data are the individual or combined facts that are out of context and have little meaning. *Data in context* are the individual or combined facts that have meaning through formal data names and comprehensive data definitions. *Information* is a set of data in context that is relevant to one or more people at a point in time or for a period of time. Information has a relevancy and a time frame that data or data in context do not have.

The bottom two tiers of the value chain, data resource and information, belong to the information technology realm. The middle two tiers, knowledge workers and business intelligence, belong to the human resource realm. The top two tiers, business strategies and

business goals, belong to the business realm. The business information demand is the human resource realm's need for information from the information technology realm. It is the failure to meet this need that puts an organization at risk.

Data Disparity

The reason that most public and private sector organizations cannot adequately meet the business information demand is the growing quantities of disparate data. *Disparate data* are essentially not alike and are distinctly different in kind, quality and character. They are unequal and cannot be readily integrated to adequately meet the business information demand. A *disparate data resource* is composed of disparate data that are dis-integrated and not subject oriented. It is in a state of disarray where the low quality does not, and cannot, adequately support the business information demand.

There are four basic problems with disparate data. First, the organization at large is not aware of all the data at their disposal. Second, the organization at large does not thoroughly understand all of their data. Third, there is high data redundancy and the redundant versions of each business fact are seldom synchronized. Fourth, there is high variability in the format and content of each business fact.

Disparate data continue to be produced at an ever increasing rate due to a *disparate data cycle*. People cannot find, do not understand, do not trust or cannot access the existing data. This situation creates an uncertainty that results in people developing their own data. These new data are not formally designed, integrated with the existing data or documented, resulting in additional quantities of disparate data.

The result of the disparate data cycle is a natural, steady drift of the data resource toward increasing disparity and decreasing quality if the development is not properly controlled and managed. This natural drift includes both traditional tabular data as well as non-tabular data, such as spatial data, image data, textual data and so on. The natural drift will continue until the development, management and use of the data resource is controlled and shifted toward an integrated high-quality data resource that supports the business information demand.

The *data dilemma* is the situation where the ability to integrate data to support the business information demand is being compromised by the continued development of large quantities of disparate data. Information technology cannot provide the human resource with the information they need to become an intelligent, learning organization. The low quality of the data resource is impacting the organization's business activities.

Data Resource Quality

Many organizations talk about improving data resource quality, but few organizations really understand data resource quality. *Data resource quality* is a measure of how well the data resource meets the current and future business information demand. Improvement in data resource quality is achieved by stopping the continued development of disparate data and then resolving the existing disparate data. The data resource drift is controlled and shifted toward development of a high-quality comparate data resource.

Information quality is a measure of the ability to get the right data, to the right people, in the

right place, at the right time, in the right form, at the right cost, so they can make the right decisions and take the right actions. The first, and most important, criteria for information quality is getting the right data from the data resource, as explained in the business intelligence value chain. Therefore, improvement in data resource quality must precede any improvement in information resource quality.

Comparate data are data that are alike in kind, quality and character, and are without defect. They are concordant, homogenous, nearly flawless, nearly perfect, high quality data. A *comparate data resource* is composed of comparate data that adequately support the current and future business information demand. The data are integrated within a common data architecture and are oriented toward business subjects. Development of a comparate data rescue ultimately leads to a data resource that is stable across changing business needs and changing technology.

Data Architecture

A *data architecture* is the method of design and construction of an integrated data resource that is business driven, based on real-world objects and events as perceived by the organization, and implemented into appropriate operating environments. It contains components that form a consistent foundation across organizational boundaries to provide easily identifiable, readily available, high-quality data to support the business information demand. A *common data architecture* is a formal, comprehensive data architecture that provides the common context within which all data are understood and integrated. It is a single architecture that transcends all data that are at an organization's disposal including manual and automated data, tabular and non-tabular data and current and historical data.

A common data architecture is mandatory to stop the disparate data cycle and promote a comparate data cycle. The *comparate data cycle* is a self-perpetuating cycle where the use of comparate data is continually reinforced because people understand and trust the data, and readily share those data. Any new data not currently defined are included when necessary, but they are developed within the common data architecture, integrated with existing data and formally documented.

Developing a comparate data resource is a two-phased approach. The development of disparate data must first be stopped and then the existing disparate data must be resolved. It does little good to start resolving existing disparate data while continuing to produce additional disparate data. This approach will never lead to a comparate data resource.

Stopping Data Disparity

The continued development of disparate data can be stopped by recognizing the bad habits that lead to the development of disparate data and turning those bad habits into good practices that lead to a comparate data resource. The ten top bad habits have been identified and turned into ten good practices[3]. Best practices have been identified that lead to early successes and encourage continued development of a comparate data resource. The good practices are divided into two groups for architectural and non-architectural.

The first five good practices pertain to the data resource architecture, including:

The formal naming of data within a formal data naming taxonomy and a supporting vocabulary.

The comprehensive definition of data to maximize denotative meaning and minimize connotative meaning.

The proper data structuring of data to provide technically correct and culturally acceptable data for all audiences in the organization.

The preparation of precise data integrity rules to ensure a high-quality data resource.

Robust documentation of the data resource that is readily available to all audiences interested in developing, managing or sharing the data resource.

The second five good practices pertain to management of the data resource, including:

A reasonable data orientation that ensures the data resource is oriented toward the business that the data resource supports and includes business client involvement.

An acceptable data availability that ensures the data are readily accessible yet the data are properly protected, and privacy and confidentiality are maintained.

Adequate data responsibility through formal data stewardship and reasonable data resource management procedures to gain control of the data resource.

An expanded data vision that includes all data at the organization's disposal and a reasonable planning horizon for development of a comparate data resource.

An appropriate data recognition that targets a vested interest in the data resource, taps the existing knowledge about the data resource and emphasizes success motivation.

Resolving Data Disparity

The resolution of existing disparate data is the second phase of achieving a comparate data resource that involves a transition of the existing data resource[4]. *Data resource transition* is formally moving from a disparate data resource to a comparate data resource within a common data architecture. It formalizes the understanding of disparate data and integrates those data within a common data architecture. It is a transition process, not a migration process, because the movement to a comparate data resource is permanent. It is a discovery process that requires considerable thought, analysis, intuition, perception and a certain amount of luck due to the uncertain understanding about disparate data.

Data resource transition includes four distinct states. The *disparate data resource* is the current state in most organizations characterized by large and growing quantities of disparate data. The *formal data resource* is where disparate data are formally understood within the common data architecture. It is a non-destructive state where the data are not changed in any way, but are only understood within a common context. The *virtual data resource* is where

data are transformed between a disparate data resource and a comparate data resource in a manner that is transparent to the business client. The *comparate data resource* is where the data have been permanently transformed and the disparate data no longer exist. It is an ideal state that may take ten years or longer to achieve.

Data resource transition includes five processes. Data inventory is the process where existing disparate data are inventoried to achieve an awareness of the data that are available to the organization. Data cross-referencing is the process where the disparate data are cross-referenced to the common data architecture to achieve a common understanding of those data. The designation of preferred data sources identifies the source that contains the most current and most accurate data. The designation of preferred data variations identifies the preferred format and content of each fact in the data resource. The development of data translation schemes supports the transformation of data between preferred and not preferred data variations.

These five data resource transition processes set the stage for data transformation. *Data transformation* is the formal process of converting disparate data to comparate data within a common data architecture. It is an expansion of the traditional extract – transform – load process.

Data Extract

Target data identification is the identification of all data needed at the target location.

Source data identification is the identification of the preferred sources for the data needed at the target location.

Data extraction is taking data from the preferred sources and placing them into a data depot for transformation.

Data Transform

Data reconstruction is the rebuilding of complete historical data from audit trails or partial historical data.

Data translation is the translation of non-preferred to preferred data values according to the data translation schemes.

Data recasting is the adjustment of data values for historical continuity when there has been definitional changes in the data.

Data restructuring is the adjustment of the data structure for the target location.

Data derivation is the development of data needed at the target location that was not available from the source locations.

Data Load

Data integrity is the application of precise data integrity rules to ensure high quality data values.

Data loading is the loading of the target location with high-quality data from the data depot.

Data review is the testing of the loaded data to verify that the data transformation process was successful.

Summary

Most large public and private sector organizations are facing a real dilemma with their data resource. The quantity of disparate data is growing at an increasing rate in spite of efforts to control the disparity. At the same time, organizations need to readily integrate their data to provide information for constantly changing business activities. This dilemma is not appropriate for building an intelligent, learning organization.

The reality of this situation is that data administration is no longer effective. A high-quality data resource cannot be developed by simply administering the data. Organizations cannot continue with paralysis by analysis from data modelers or brute force physical development from technicians. They need formal data resource management where data architects and data engineers work together to develop a high-quality data resource. They need to manage their data resource equivalent to the management of finances, physical property and human resources.

The fundamental approach to formal data resource management is to understand, manage and share all data that are at an organization's disposal within a single, organization wide, common data architecture. Understanding data within a common context starts a cycle of increased data sharing and improved data quality. When data are understood they are readily shared which improves their quality. The improved data quality promotes additional data sharing. Once started, this data sharing – data quality cycle drives the development of a comparate data resource that meets the current and future business information demand.

Mr. Brackett is the founder of Data Resource Design & Remodeling and is currently the President of DAMA International. He helps public and private sector organizations develop an organization-wide integrated data resource, stop the continued production of disparate data and resolve existing data disparity. He has written numerous books and articles and is a prominent speaker at national and international conferences. His latest book *Data Resource Quality: Turning Bad Habits into Good Practices* describes ten steps to stop the creation of disparate data. Further information can be found at members.aol.com/mhbrackett. Mr. Brackett can be reached at mhbrackett@aol.com.

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FACT AND FICTION IN ENVIRONMENTAL DATA QUALITY

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Environmentally related decisions on public policy have a tremendous impact on the lives of the affected population in terms of their potential to prevent, allow or cause adverse health effects, ecological damage and economic expense. However, data about the state of the environment or the potential health, ecological or economic impact of alternatives being considered in a situation is inherently less than perfectly accurate and often incomplete. The definition and presentation of quality for environmental data presents challenges that stem from the very nature of the methodology used to obtain the data. Physical measurements are subject to inherent error in the selection of a sample to represent a population under study, the measurement device itself and processing of the raw data for interpretation. In addition, environmental data is fundamentally tied to time and location constraints, which limits its applicability outside of their limited spatio-temporal domain.

More often than not, data is collected specifically for a project because there is no data available in sufficient quantity and quality to meet the requirements of the pending decision. In some cases, a repository of data is made available to a group of data users for the purpose of analysis and decision making (i.e., a “data resource” or “data warehouse”). It is not unusual to assemble a dedicated data resource for a national environmental program or even for environmental management at a Federal facility, or for a large environmental project. When planning and assembling a data resource for environmental use, data quality is a critical concern because of the issues at stake and the consequences of making a wrong decision. The goal of generating and storing data that has intrinsic quality no matter what future use it may be given is unattainable. A common objective for quality of environmental data is for it to be of known quality and appropriate for its intended use. Representation of quality statements and limitation on usability of the data should be built into design of the data resource.

Common approaches to quality assurance for business-oriented data resources fall short when applied to environmental data resources because of the need to define quality differently. The inherent uncertainty on environmental data can be dealt with by applying practical approaches to the particular situation. Example applications of common types of data encountered in environmental data resources including their inherent problems and approaches for solutions are discussed. Applications include spatially or temporally distributed data, chemical or biota analysis results, biological field observations and geophysical measurements.

HPLC/MS METHODS USING ELECTROSPRAY AND APCI INTERFACES

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No abstract available.

THE NEW ROLE FOR LC/MS AND LC/MS/MS IN EXPLOSIVES INVESTIGATIONS

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Introduction

Liquid chromatography/mass spectrometry (LC/MS) is an instrumental technique that has been applied to the analysis of explosives for many years. Our laboratory has used LC/MS for explosives testing for approximately 10 years. Older LC/MS instruments provided detection limits comparable to the conventional HPLC/UV method (EPA Method 8330) and were more selective. However, because of the comparatively higher cost, the primary role for LC/MS was confirmation of samples in which interfering chemicals made interpretation of HPLC/UV results difficult. This is changing. Advances in LC/MS instrumentation afford limits of detection 10-20 times or more lower than before. This, combined with lower risk-based PRGs, new regulatory concerns and encroachment of communities into the immediate vicinity of military sites, has created a new role for LC/MS as the primary method for definitive analysis in some explosives investigations. Recent examples will be presented in which a common military site contaminant and biogenic substances created analytical difficulties effectively solved by LC/MS and LC/MS/MS.

Most explosive compounds or explosive related compounds have unique physical and chemical characteristics that make them unsuitable for analysis by the conventional EPA gas chromatography (GC) methods. They are relatively polar, but have low solubility in water. They have a low vapor pressure, but tend to be heat labile, i.e., they tend to break down at temperatures typically used in GC injectors. Liquid chromatography (LC) methods are well suited to the analysis of polar, non-volatile and heat sensitive compounds. In general, LC can be used for analysis of a much wider range of compounds than is possible by GC methods. As a result, the standard method for analysis of explosives has been EPA Method 8330, which uses dual column high pressure liquid chromatography (HPLC) with an ultraviolet (UV) detector. The method detection limits (MDLs) for water samples analyzed by Method 8330 are approximately 0.1 to 0.2 µg/L for most compounds.

Another HPLC instrumental technique that has been used for many years is LC/MS with a thermospray interface, EPA Method 8321. Using the thermospray interface, the older mass spectrometers, produced MDLs roughly equivalent to those obtained by Method 8330, 0.1 to 0.3 µg/L. The advantage to the LC/MS technique is that the mass spectrometer is a much more selective detector. It can resolve low concentrations of the explosive compounds in the presence of co-contaminants and interferences that defeat analysis by UV detector, whether fixed wavelength or the more modern diode array (DAD). Using tandem mass spectrometers (LC/MS/MS), it is possible to detect compounds while establishing information about the chemical structure of the compounds being tested, which is not possible with a UV detector. However, LC/MS equipment is more expensive than HPLC/UV, the equipment requires considerably more maintenance than the standard HPLC/UV and the level of training and experience required of the operator is much higher. As a result, the cost of an analysis for explosives by LC/MS is higher than by HPLC/UV, and so LC/MS was most often relegated to

the role of confirming HPLC/UV results for difficult samples. HPLC/UV was invariably the method of choice for definitive analysis explosives where interferences were not a significant problem.

New LC/MS Capability

The situation is changing in part because of the development of commercial LC/MS equipment using electrospray and/or atmospheric pressure chemical ionization (APCI) interfaces. These interfaces apply less energy to the spray coming out of the HPLC column, i.e., they use a softer ionization technique, which can result in less fragmentation of the compounds being analyzed. Unlike the older thermospray interface, the newer interfaces produce the molecular ion or adducts of the molecular ion for the explosives at greater than 90% abundance. Modern LC/MS/MS equipment is also more efficient in transporting the ions created at the interface into and through the mass spectrometer, which makes analysis at the second quadrupole more efficient. The result is that the sensitivity of LC/MS and LC/MS/MS for the analysis of explosive compounds has recently improved by a factor of ten to twenty times. LC/MS and LC/MS/MS instruments are now capable of detecting explosive compounds at levels more than an order of magnitude below levels that can be detected by the standard HPLC/UV method. This is apparent in the example in Figure 1, which shows HPLC/UV and LC/MS chromatograms for a 10 µg/L calibration standard containing HMX and RDX. The same C18 column was used on both instruments. The LC/MS signal for both HMX and RDX are well above background noise levels, whereas the HPLC/UV signal is marginally above background levels.

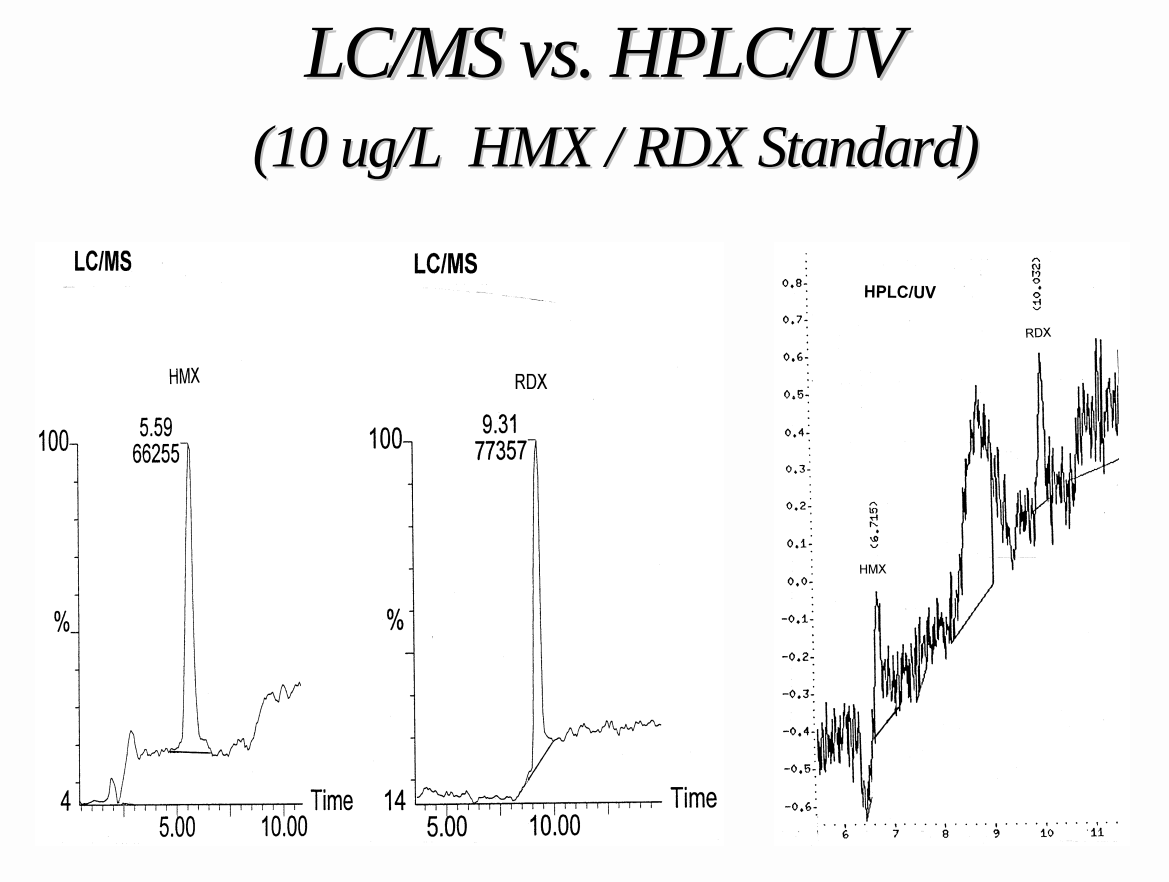

Figure 1

New Risk Levels

The role of LC/MS in explosives investigations is also being driven by new risk levels. Through the 1990s new toxicology data was made available to the EPA resulting in lower risk levels assigned to tap water and groundwater sources that might be drinking water sources. As an example, the EPA Region IX Preliminary Remediation Goal (PRG) for 2,4-dinitrotoluene was changed from 73 µg/L to 0.099 µg/L, a 740 times decrease from earlier years. Toxicological studies are incomplete for many compounds, particularly the amino and nitroso breakdown products of the most commonly used explosives, TNT and RDX. At some military sites, remedial action levels are being set at these new lower risk levels for the conventional explosive compounds and levels are being considered for others. As shown in Figure 2, there are perhaps seven explosive compounds with levels of interest for remedial investigation studies that are below the quantitative limits of HPLC/UV and the older LC/MS technology. In the case of at least three of the compounds (2,4-dinitrotoluene, 2,6-dinitrotoluene, and 1,3-dinitrobenzene), current risk levels are below limits of detection for the HPLC/UV and older LC/MS technology.

Risk-Based Water Cleanup Levels vs. Sensitivity for LC/MS & HPLC/UV

(in order by concentrations of concern) *STL Denver*

	----------Risk/Cleanup Criteria----------				--Methods of Analysis--	
	EPA Region IX Tap Water PRG 11/22/00 update (µg/L)	USEPA IRIS $1x10^{6}$ Risk (µg/L)	USEPA DW Sources $1x10^{6}$ Risk (µg/L)	1999 Cleanup Levels (µg/L)	LC/MS SPE / 8321A MDL (µg/L)	HPLC/UV SPE / 8330 MDL (µg/L)
HMX	1800.00	---	---	602.00	0.02	0.10
1,3,5-TNB	1100.00	---	---	361.00	0.02	0.06
PETN	---	---	---	---	0.02	0.80
2-amino-DNT	---	---	---	168.00	0.01	0.10
4-amino-DNT	---	---	---	120.00	0.02	0.20
Tetryl	---	---	---	120.00	0.02	0.10
2-Nitrotoluene	61.00	---	---	118.00	0.02	0.08
3-Nitrotoluene	61.00	---	---	118.00	0.02	0.20
4-Nitrotoluene	61.00	---	---	118.00	0.02	0.20
Nitrobenzene	3.40	0.35	3.50	3.50	0.02	0.10
TNT	2.20	1.00	---	2.01	0.05	0.08
RDX	0.61	0.30	---	0.55	0.03	**0.20**
MNX	---	---	---	---	0.01	**0.20**
DNX	---	---	---	---	0.01	**0.20**
TNX	---	---	---	---	0.03	**0.20**
2,4-DNT	0.10	0.05	0.11	0.09	0.02	**0.10**
2,6-DNT	0.10	0.05	---	0.09	0.01	**0.20**
1,3-DNB	0.10	---	---	1.20	0.02	**0.10**

Notes: MDLs ≥ 1/3 of cleanup levels are highlighted (3xMDL = ACS Limit of Quantitation)

DW = Drinking Water
GW = Ground Water
IRIS = Integrated Risk Information System
MDL = Method Detection Limit Study performed at STL Denver per 40CFR136B
MNX, DNX, & TNX preliminary levels of interest equivalent to RDX per EPA Region X
PRG = Preliminary Remediation Goal
SPE = Solid Phase Extraction, EPA Method 3535
1999 Cleanup Levels = Action levels for one active Army site
DNB = Dinitrobenzene
DNT = Dinitrotoluene
DNX = 1,3-Dinitroso-5-nitro-1,3,5-triazacyclohexane
HMX = Octahydro-1,3,5,7-tetranitro-1,3,5-triazine
MNX = 1-Nitroso-3,5-dinitro-1,3,5-triazacyclohexane
PETN = Pentaerythritol tetranitrate
RDX = Hexahydro-1,3,5-trinitro-1,3,5-triazine
TNB = 1,3,5-Trinitrobenzene
TNX = 1,3,5-Trinitroso-3,5-dinitro-1,3,5-triazacyclohexane

Figure 2

Short Case Study

For many years, the STL Denver laboratory has been involved in remedial investigation studies at an U.S. Army munitions site built in World War II. The need for environmental studies at and around the site was recognized in the 1980s and earlier. Regulatory actions to investigate the full extent of contamination was delayed 15 years due, in part, to concerns with unexploded ordinances (UXOs). During those years, to an extent even today, focus was on UXO detection and soil characterization related to UXOs.

As soon as EPA Method 8330 was promulgated in 1989, it became the method of choice for definitive analysis of explosives at this site. RDX and TNT were the primary compounds of concern. Colorimetric and immunoassay methods were put into use as soon as they became available (1990-1995), and they continue to be used as field screening methods.

In the mid-1990s concern about groundwater downgradiant from the site began to grow in the nearby community. The community had grown over the years, and land immediately adjacent to the fence line of the site is in use. Studies found that particles of TNT remained on the surface for decades. RDX proved to be persistent and mobile once dissolved in rainwater percolating into the water table.

Action levels were lowered in the late 1990s to the levels shown in Figure 2. 8330 MDLs were then near or above levels of concern. In late 2000 state regulators began to demand quantitative results at or below action levels. As a result, in 2001 LC/MS and LC/MS/MS became the definitive method for groundwater characterization, and our laboratory was certified by the U.S. Army Corps of Engineers for analysis of explosives using LC/MS and LC/MS/MS.

Two Example Applications

Early this year, we tested a groundwater sample from the site containing 10 mg/L of JP4 jet fuel. Figure 3 shows an HPLC/UV chromatogram for the sample alongside a chromatogram for a laboratory control sample (LCS) run immediately before the sample on the same instrument. Although peaks were detected in the first 13 minutes of the sample chromatogram and the baseline was elevated, this appeared to be due to material from the JP4 because no explosive compounds were detected. Figure 4 shows an LC/MS chromatogram for the same sample, with a peak for RDX easily detected at 0.05 µg/L.

Groundwater with 10 mg/L Jet Fuel (JP4) by HPLC/ UV

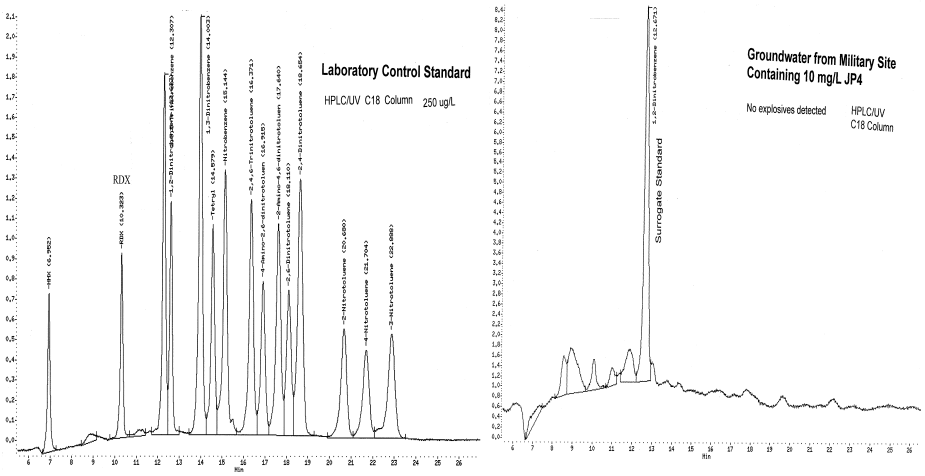

Figure 3

GW with 10 mg/L Jet Fuel (JP4) Analyzed by LC/MS

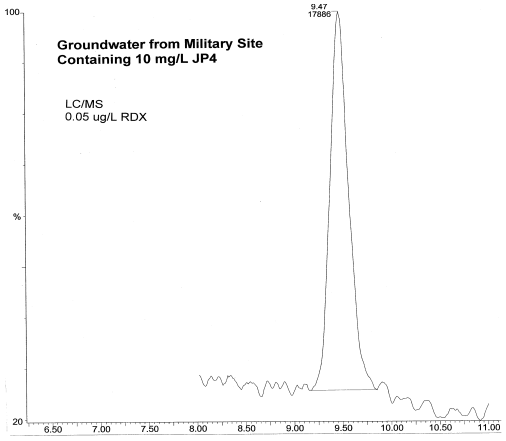

Figure 4

Also this year, we were asked to test an acetonitrile extract from plant tissue. The extract had been prepared from a cleaned and freeze dried sample prepared by the U.S. Army Waterways laboratory. We were told that an earlier analysis using older LC/MS instrumentation had detected low concentrations of RDX and 2,4,6-trinitrotoluene (TNT) in the extract. We were asked to confirm those results. Using an HPLC/UV we first obtained the chromatogram shown in Figure 5. A number of poorly resolved peaks were detected, but no explosives were identified. Using a Micromass Quattro Ultima tandem mass spectrometer operated with an

APCI interface in the negative ion mode we obtained the single ion chromatograms shown in Figure 6. The 281 amu RDX parent ion was detected, but not the required 46.15 amu daughter ion; the RDX detection by the older LC/MS was not confirmed. However, the TNT result was confirmed. Both the parent ion and the required 109 amu daughter ion were detected. Subsequently the laboratory performed a spike addition experiment by adding a known amount of RDX and TNT to the extract and reanalyzing. The extract spiked with RDX produced a peak at 46.15 amu and a split peak pattern at 59.1 amu, indicating that the compound in the unspiked sample was similar to, but not RDX. The extract spiked with TNT produced a single peak, with a recovery of 115%, which further confirmed the presence of TNT. Surprisingly, the analysis indicated that the original dried plant tissue contained approximately 7 mg/kg of TNT.

Plant Tissue from Phytoremediation Analyzed by HPLC/UV

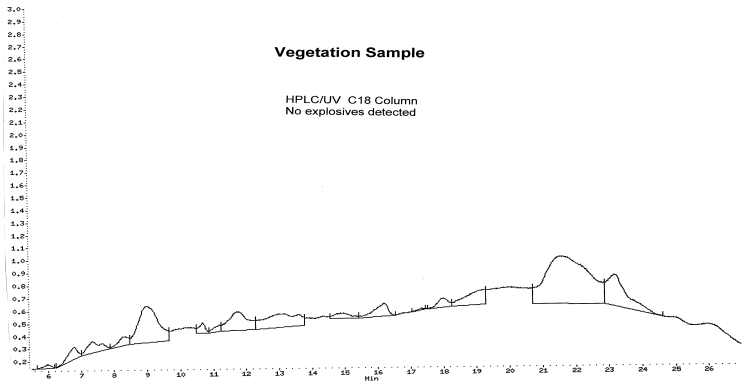

Figure 5

Analysis of Plant Tissue by LC/MS/MS

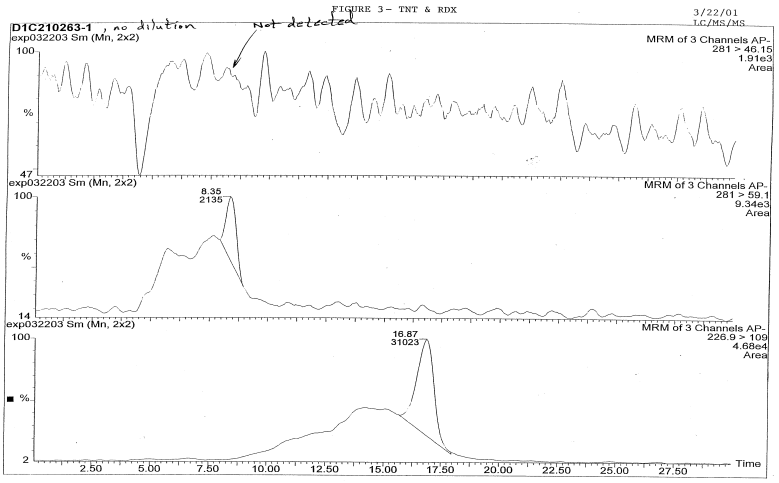

Figure 6

Conclusion

Our laboratory continues to explore interesting and new applications of this powerful new analytical tool. Analysis of the amino and nitroso degradants of the explosives as markers for contaminant plumes is one application we are pursuing. Clearly there is a need for this more sensitive explosives compound method in groundwater studies. This need is driven by

- the awareness of the longevity of some explosives compounds,
- the growing awareness of the mobility of some explosives,
- new regulations, e.g., the Munitions Rule,
- community involvement in remedial investigations, and
- the new risk levels.

Obviously the older field methods and the conventional HPLC/UV method will continue to play a key role. However, our own experience has shown that LC/MS and LC/MS/MS analysis using the newer instruments are the only established techniques for difficult real-world samples requiring both a high degree of sensitivity and accuracy.

THE ANALYSIS OF CARBAMATES USING LC/MS

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ABSTRACT

The analysis of carbamates has received renewed interest recently in light of their implication as potential endocrine disrupters, and their use as common pesticides for food products. Before their use, carbamates must be manufactured from various raw materials that are themselves potential endocrine disrupters, and the manufacturing waste must be characterized prior to disposal. All total, carbamates and related products are entering into eco-system with potential adverse effects.

The EPA Office of Solid Waste has recently published a final rule covering the analysis of 40 carbamate waste constituents. To monitor all these currently requires 6 different analytical methods from GC to LC. Several of the listed carbamate methods utilize mass spectrometry (MS) detection.

This presentation will discuss the development of a single, multi-analyte analysis of several commonly used carbamates, their precursors and degradation products using HPLC-Positive/Negative Electrospray Mass Spectrometry. For non-MS detection methods, analyte resolution is critical for identification and quantitation. However, the capability of MS to detect a single m/z ratio gives analyte detection specificity that does not require chromatographic resolution. Simultaneously, the capability to program different cone voltages with respect to time gives the ability to fragment the analyte, called collision-induced disassociation (CID), which aids in positive analyte identification.

This work will shed insight into how new mass spectrometry technology can be applied to enhance the monitoring of environmental carbamate pollutants as well as other organics.

INTRODUCTION

Carbamates are commercially available pesticides derived from carbamic acid. Highly effective and having a broad spectrum of activity, carbamates are used worldwide to protect crops and other vegetation from the ravages of insect pests.

Carbamates, their intermediaries, their degradation products and their metabolites are of great concern to members of the regulatory and scientific communities as more and more drinking water sources are testing positive for the presence of carbamates. They find their way into the aquifers and surface water through agriculture runoff after being directly applied to food crops such as grains, fruits and vegetables. If food crops are harvested too soon after application,

residues and their by-products may remain on the produce. Additionally buyers of grain, fruits and vegetables are becoming increasingly vigilant for pesticide residues due to their toxic nature.

In an effort to protect drinking water resources, the U.S. Environmental Protection Agency and other international governing bodies now regulate pesticide use and require routine monitoring of drinking and raw source water. This effort has been extended to solid waste products such as soil and hazardous waste disposal, all of which could potentially contaminate the drinking water supply.

EXPERIMENTAL

In this study, various instrumental and chromatographic conditions were examined and optimized for the analysis of a ~50 carbamate component standard mixture without the use of post column derivatization.

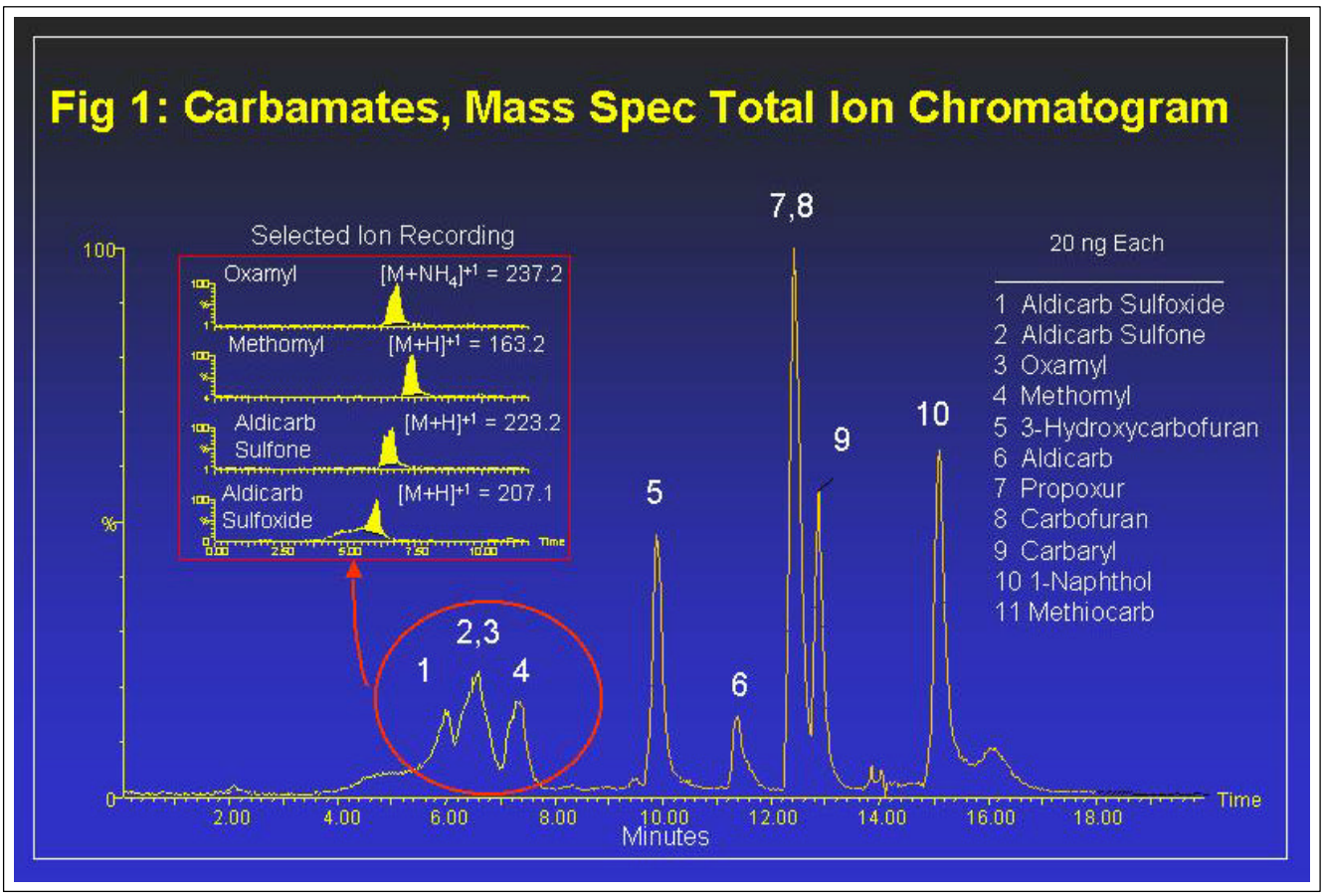
System:	Waters Alliance® LC/MS with MassLynx™ system control & data processing
Mass Spec:	Waters ZQ Detector (Single Quad with 2000 amu mass range)
Ionization Mode:	Positive Electrospray (ESI^+)
Column:	Waters Symmetry® C_{18}, 3.5 µm, 1 mm x 150 mm
Temperature:	35° C
Mobile Phase:	Linear Gradient using AcCN / 10 mM NH_4 Acetate
Flow Rate:	100 µL/min
Injection Vol:	20 µL/min

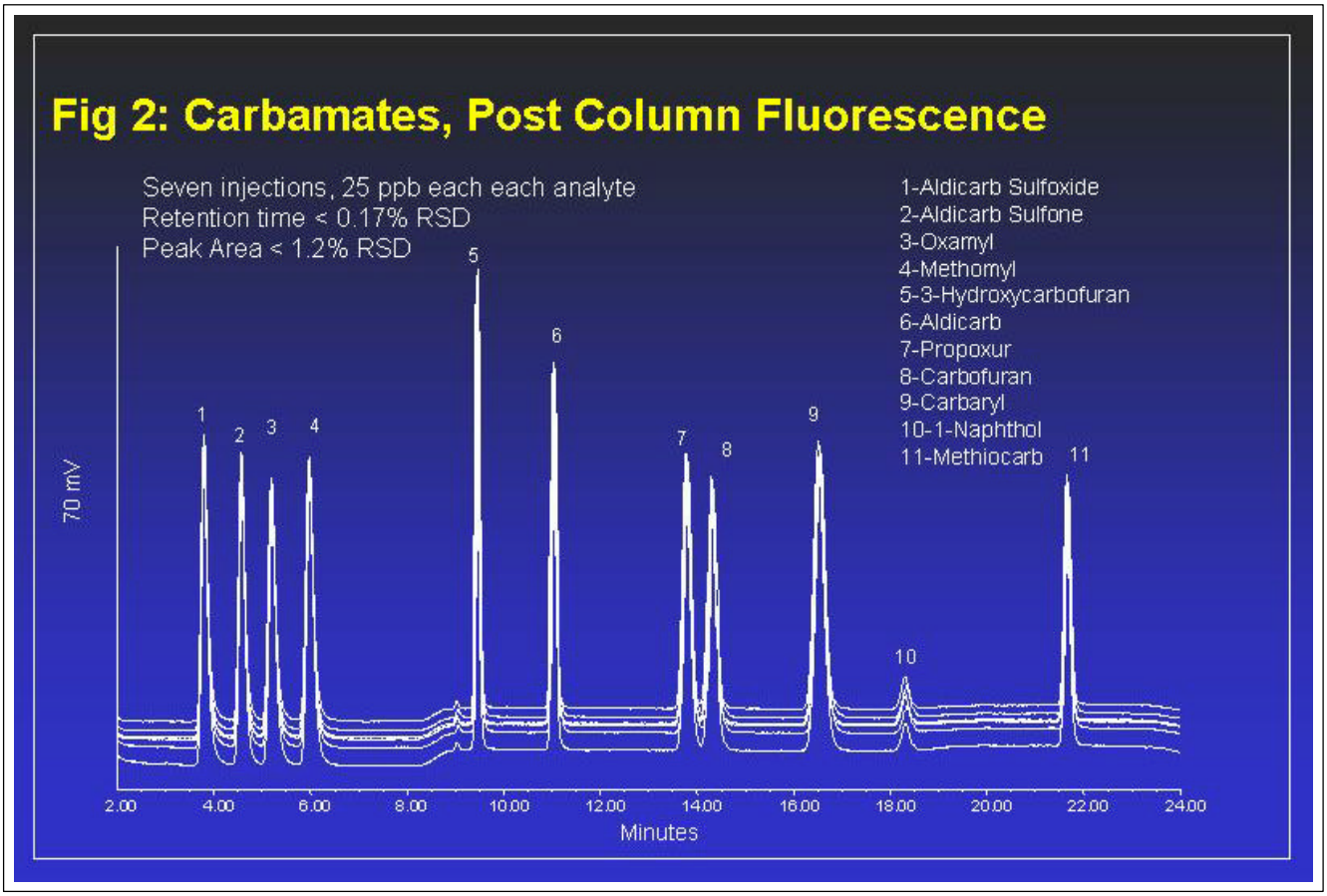
The carbamates working standards were provided by EPA Office of Solid Waste, as 0.1 mg/mL concentration in MeOH. Dilutions to 1 µg/mL were made with 100% MeOH. Calibration standard dilutions were made with DI water

DISCUSSION

The new multi-analyte screening method is based upon preliminary work discussed below, and gives credibility and justification to extend the scope of the method to include additional carbamate analytes.

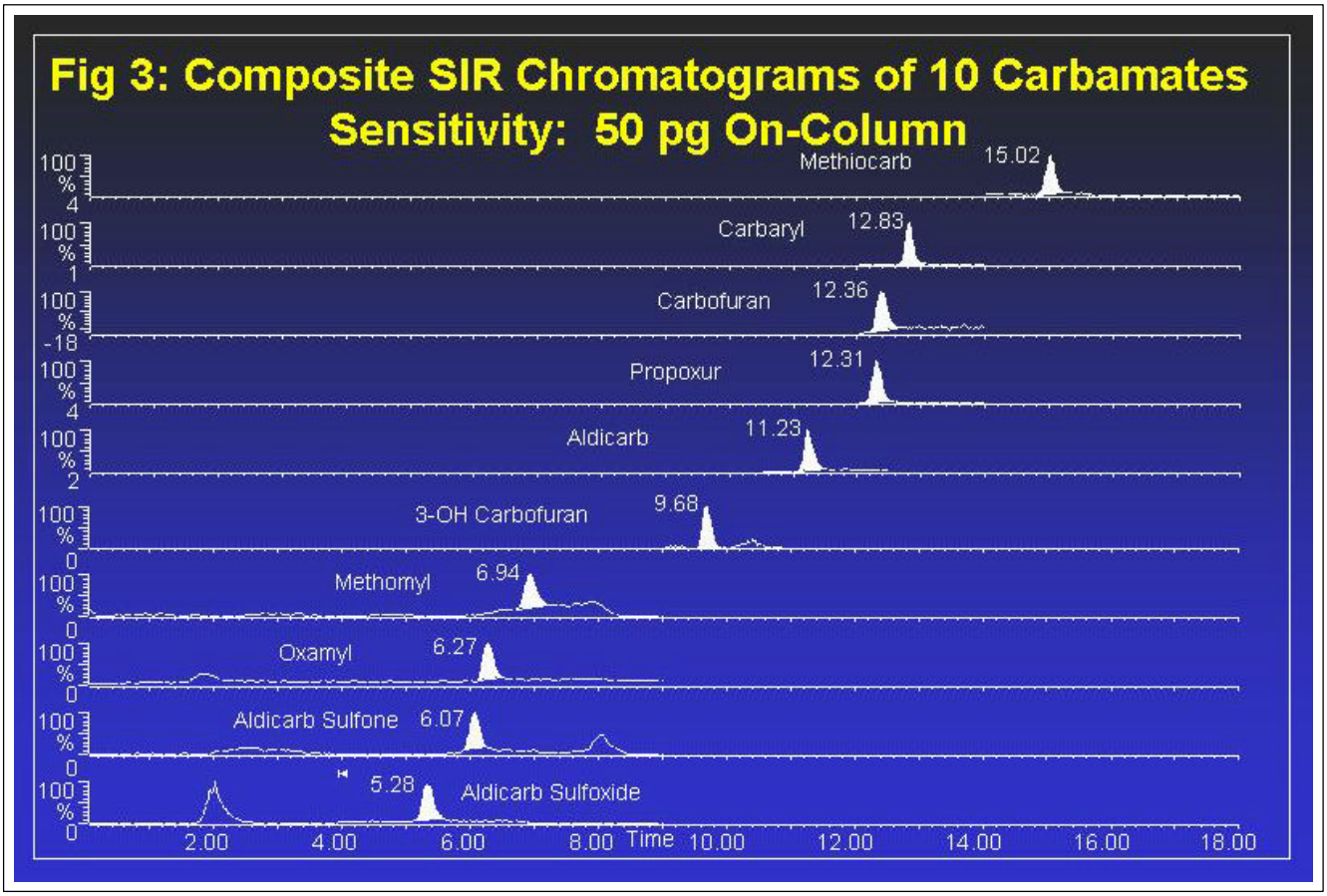
Figure 1 shows the total ion chromatogram (TIC) from the full scan analysis of 20 ng (10 µL of 2 µg/L) of each of a 10 component carbamate mixture using a linear gradient of MeOH/NH_4 acetate. Another carbamate standard at 10 mg on column was analyzed using the post column fluorescence method, with different column and gradient profile, and is shown in Figure 2. Note with the MS TIC, the first four carbamates coelute, but are fully resolved with the post column method. For conventional carbamate identification and quantitation using UV or fluorescence, carbamate resolution is critical. However, for mass spectrometry, resolution is not as critical.





By extracting from the full scan, the $[M+H]^+$ or $[M + NH_4]^+$ ions specific to each coeluting compound, individual chromatograms can be resolved by the mass spectrometer, as shown in the insert of Figure 1. This allows for other unknown carbamates or organics in a complex matrix, such as wastewater or solid waste, to be selectively detected, identified and quantitated without the need for chromatographic resolution.

The carbamate mixture was re-analyzed and acquired in the SIR (single ion recording) mode, where the MS detector was set to detect only a single $[M+H]^+$ ion value for each analyte, Figure 3. Each chromatogram only shows the single, individual carbamate in the mixture, and demonstrates the selectivity of mass spec detection. Concurrently, acquisition in the SIR mode also enhances sensitivity. These are the primary benefits of mass spec detection.



A series of 6 carbamate working calibration standards between 5 and 1000 ng/mL (ppb), representing between 50 and 10,000 pg on column, were analyzed in triplicate, and calibration curves generated using SIR response and a 1/x weighting. The 1/x weighting was used to minimize the statistical effect of the higher concentrations on the linear regression. The coefficient of determination, given in Table 1, for the weighted regressions was >0.995. Again, this demonstrates that resolution is not as important with MS detection as it is with conventional detection.

The lowest carbamate calibration standard, 5 ng/mL (ppb) or 50 pg on column, was analyzed five times to calculate the limit of detection, defined as three times the standard deviation, the limit of quantitation, defined as 10 times the standard deviation, and the precision, defined as %RSD = (mean)(100)/std dev). This data is tabulated in Table 1.

Table 1. Mass Spec Carbamate Linearity, Sensitivity and Precision

Carbamate	Coefficient of Determination r^2	Limit of Detection ng/mL (ppb)	Limit of Quantitation ng/mL (ppb)	Response for 50 pg %RSD
Aldicarb Sulfoxide	0.9969	0.8	2.6	3.5
Aldicarb Sulfone	0.9982	1.8	6.1	9.6
Oxamyl	0.9990	0.7	2.2	3.2
Methomyl	0.9959	1.6	5.5	10.0
3-OH Carbofuran	0.9970	0.4	1.4	2.1
Aldicarb	0.9963	0.2	0.5	0.7
Propoxur	0.9963	0.7	5.5	11.3
Carbofuran	0.9981	0.9	3.0	7.5
Carbaryl	0.9994	0.3	1.1	1.8
Methiocarb	0.9995	0.4	1.4	2.0

Single quad electrospray MS is generally optimized to detect the parent analyte MW ion and little if any fragmentation, or daughter ions, as is the case with electron impact ionization used with GC/MS. However, by increasing the MS cone voltage, limited fragmentation can be achieved, known as collision induced disassociation (CID) shown in Figure 4. Here, methomyl is fragmented into two daughter ions, 88 and 106, specific to methomyl. By employing the “three ion rule”, the abundance ratio of daughter ion to parent ion is “relatively” constant as shown in Figure 5, and from these ratios positive analyte identification can be determined. However, this is a topic of considerable controversy.

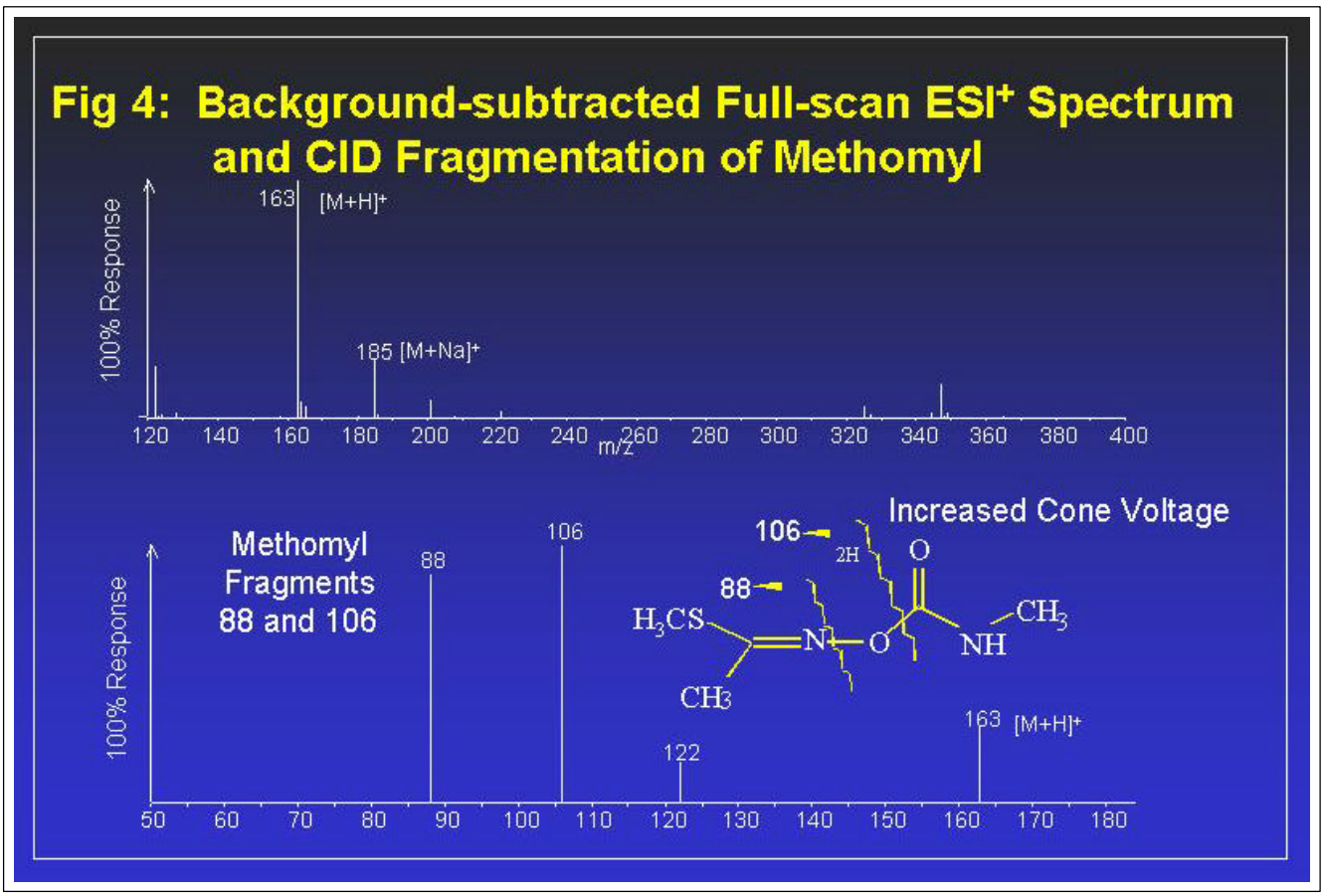


Fig 5: Methomyl Confirmation in Spinach "Three-Ion Rule"

	Standard			Spinach		
Ion m/z	88 Da	106 Da	163 Da	88 Da	106 Da	163 Da
% Relative Abundance	100	51	34	100	55	34
	100	56	36	100	62	36
	100	54	34	100	55	30
	100	51	32	100	65	35
	100	55	31	100	63	36
	100	52	30	100	65	37
	100	54	30	100	69	38
	100	54	30	100	71	37
	100	54	30	100	72	38
	100	55	30	100	51	31
Mean	**100**	**53.6**	**31.7**	**100**	**62.8**	**35.2**
S.D.	**-**	**1.71**	**2.21**	**0**	**7.16**	**2.78**
% C.V.	**-**	**3.2**	**7.0**	**0**	**11.4**	**7.9**

CONCLUSION

These data indicate that the use of single quad electrospray mass spec detection is a viable technique for the analysis of carbamates. The carbamate detection limit and precision show that this electrospray method gives equivalent results to the validated thermospray MS method described in 8321A. Thus, LC/ mass spec technology can be extended to a multi-analyte carbamate screening method.

STRONG START FOR NELAP

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Recent Accomplishments

EPA's National Environmental Laboratory Accreditation Program (NELAP) announced the first group of 669 NELAP-accredited laboratories on January 24, 2001, which flags an end to a decades long problem of non-uniform state accreditation programs. The announcement of these 669 laboratories is a strong beginning for a national program. Although only eleven states have adopted the standards, the laboratories represent a much larger cross section - 38 states/territories and 3 foreign countries. Several hundred more laboratories are expected to become NELAP-accredited before the end of the year. Additional states and federal agencies will expand the number of NELAP accrediting authorities in the near future. Names and contact information for the NELAP accredited laboratories are published on the National Environmental Laboratory Accreditation Conference (NELAC) website (http://www.epa.gov/ttn/nelac).

What is NELAC?

NELAC is a voluntary association of State and Federal agencies formed to establish and promote mutually acceptable performance standards for environmental laboratories. Private sector input to the process is obtained through a variety of mechanisms including open semi-annual meetings, committee participation and the Environmental Laboratory Advisory Board (ELAB), a federally charted committee that provides consensus advice from a balanced representation of the private sector.

Although formally established in 1995, the efforts to develop NELAC began in 1990, when the private sector petitioned EPA Administrator Lee Thomas for assistance in developing a solution to the multiple problems resulting from the lack of a national program; such as inconsistent requirements, lack of reciprocity and redundant on-site assessments and proficiency tests. Since then all EPA administrations have continued to support the program, which is based on a strong federal-state partnership designed to include private sector input at every step. There was a relatively brief feasibility study by EPA, followed by a two year evaluation of options by a federal advisory committee and finally a State/EPA committee that developed the original draft standards.

Just as the private sector was instrumental in initiating NELAC, they have been equally involved in developing the standards, serving on 12 different committees. In order to be fully compliant with the Federal Advisory Committee Act, the private sector cannot have a voting role. Their knowledge, experience and hard work, however, have contributed tremendously to the standards and have had significant impact.

What is the future of NELAC?

EPA is committed to providing its current, low level support while the NELAC Board of Directors explores alternate funding and support. NELAC enjoys the strong support of the states and the vast majority of the non-regulatory stakeholders. Additional accrediting

authorities are expected to adopt the NELAC standards in the near future. It is estimated that, within 12 months of the announcement of the first group of 669 laboratories, the number of NELAP accredited laboratories will more than double.

NELAC QUALITY SYSTEMS: THE INTEGRATION OF ISO/IEC 17025 AND PBMS

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Abstract
Within the past year the National Environmental Laboratory Accreditation Conference (NELAC) Quality Systems Committee has been working on a major restructuring of the quality systems standards to integrate the ISO/IEC 17025 international standard and performance-based measurement system (PBMS) concepts (i.e., additional flexibility) into the present standards. This paper will provide the rational for that effort and will give an update on the status of the Committee's activities in this and other key areas. Further, the paper will provide an overview of a key section of the present draft language, that relates to ISO/IEC 17025 and PBMS, for the NELAC Quality Systems chapter.

INTRODUCTION

The adopted June 29, 2000, NELAC Quality Systems standards (i.e., NELAC Chapter Five) are based on ISO/IEC Guide 25. NELAC has also stated its commitment to the use of Performance-Based Measurement Systems (PBMS) in environmental testing and toward providing a foundation for PBMS implementation in the standards. Hence, with the advent of ISO/IEC 17025 as the replacement for ISO/IEC Guide 25 and the Environmental Laboratory Advisory Board's (ELAB) PBMS Straw Model (presented at NELAC VII) the NELAC Quality Systems Committee has begun efforts to develop proposed language for NELAC Chapter 5 that would integrate both ISO/IEC 17025 and the PBMS Straw Model concepts/elements into the standards. Obviously, the NELAC Quality Systems Committee initiation of this effort was done with the knowledge and support of both the NELAC Board of Directors and ELAB. The draft work done on these efforts was presented and discussed at NELAC VII (May 2001) during the Quality Systems Committee session. Actual proposed language for these changes will be presented at NELAC VIII (December 2001).

The primary goal of this effort is to improve overall quality of compliance data via the NELAC quality system standards. The Committee views the incorporation of the superior ISO/IEC 17025 international standard as its base and further utilization of a PBMS approach for performing environmental analyses under NELAC as a means to do just that: improve data quality. Additionally, many NELAC stakeholders view this integration effort as a means to bring about some positive and needed improvements in the current NELAC Chapter 5 language.

CURRENT ACTIVITIES AND DIRECTION

During NELAC VII (November 2000) the NELAC Quality Systems Committee discussed its ISO/IEC 17025 integration efforts and also formed a PBMS Subcommittee to address the PBMS Straw Model. The NELAC Quality Systems Committee's ISO/IEC 17025 integration efforts were essentially delayed between NELAC VI and NELAC VII due to ongoing ISO/IEC 17025 copyright and copyright licencing fee issues that NELAP had with ANSI. Those issues are still being considered by the NELAC Board of Directors and have had an impact on the

direction the Quality Systems Committee has taken. Essentially both the above NELAC Quality Systems Committee efforts got underway only after NELAC VII.

The NELAC Quality Systems Committee has as part of its ISO/IEC integration effort initially developed a spreadsheet that contrasts ISO/IEC 17025, NELAC Chapter 5 and ISO/IEC Guide 25 elements. This tool provided direction on the Committee's next steps. The Committee then identified the current ISO/IEC Guide 25 language in NELAC Chapter 5 for possible removal. The Committee has also inserted the present Chapter 5 language under the appropriate/corresponding ISO/IEC 17025 section since the ISO/IEC 17025 language will provide the framework for any revised Chapter 5. Lastly, due to the ANSI copyright issue, the Committee was also directed to be ready to provide a version of NELAC Chapter 5 that would only cite ISO/IEC 17025 by reference.

Prior to NELAC VII, the Committee was working on drafting a revised NELAC Chapter 5 version that would have ISO/IEC 17025 sections as the main framework (yet structured as to be able to cite these sections by reference only if needed) with current and revised NELAC Chapter 5 language (either minus the old ISO/IEC Guide 25 language or with the ISO/IEC Guide 25 language highlighted) inserted where appropriate. Further, this revised NELAC Chapter 5 version would have inserted in it the revised sections of NELAC Chapter 5 that the PBMS Subcommittee is working on. The goal was initially to have this document ready for proposal at NELAC VII (May 22-25, 2001), but the extent and depth of the undertaking did not allow us to make the imposed March 19, 2001 deadline for Committees to submit final proposed language to the NELAP Director.

ELAB's PBMS Straw Model which was heavily influenced by ISO/IEC 17025's Section 5.4 (Test and Calibration Methods and Method Validation) as it relates to how laboratories should implement and use laboratory methods brought two key concepts to the table. The two most significant concepts that have influenced the PBMS Subcommittee's efforts are:

Method Selection; and
Method Validation.

The PBMS Subcommittee early on identified NELAC Chapter 5's sections 5.10 (Test Methods and Standard Operating Procedures), 5.9.4 (Calibration), and Appendix C (Demonstration of Capability) as important areas to revise to address the PBMS Straw Model concepts/elements. To date the PBMS Subcommittee has essentially completely rewritten Chapter 5 section 5.10 and Appendix C. As part of this effort the PBMS Subcommittee anticipates additional changes will be needed to Appendix D.1 (Chemical Testing) that what was voted on and adopted at NELAC VII. Significant revisions have been drafted for sections 5.9.4 (Calibration) and a few changes in section 5.5.4 (Quality Manual) and elsewhere in the main body of Chapter 5. The main changes revolve around sections 5.10 and Appendix C.

Again, at NELAC VII the Quality Systems Committee's ISO/IEC 17025 integration effort and the PBMS Subcommittee's efforts were presented publically for the first time via presentations and a discussion document (note the PBMS Subcommittee's discussion document was not to be put for a vote at NELAC VII) during the NELAC Quality Systems session. Per a straw poll, there was broad support expressed by NELAC stakeholders at NELAC VII (i.e., states, federal

agencies and the private sector) for the full integration of ISO/IEC 17025 into NELAC Chapter 5.

The NELAC Quality Systems Committee did bring to NELAC VII, as proposed language and put up for a vote, the Committee's rewrite of Appendices D.1 (Chemical Testing) and D.3 (Microbiology Testing). The D.3 proposed language was discussed at NELAC VII and the D.1 proposed language is based on the ELAB's May 2000 proposed revisions to D.1. The ELAB's May 2000 proposed changes to D.1 were publically discussed and widely supported at NELAC VII as part of the NELAC Quality Systems Session. The proposed changes to D.1 and D.3 were adopted at NELAC VII with minor modifications (e.g., Method Blank Criteria). The standards that came out of NELAC VII were to be posted at the end of June 2001 on the NELAC Homepage website at: http://www.epa.gov/ttnnela1/.

LANGUAGE THAT RELATES TO ISO/IEC 17025 & PBMS STRAW MODEL

Obviously, with possibly bringing the entire ISO/IEC 17025 international standard into NELAC Chapter 5, there would be new language that would represent some changes from the current ISO/IEC Guide 25 based Chapter 5. While ISO/IEC 17025 has more emphasis/detail in the technical requirements there appears to be greater flexibility within ISO/IEC 17025.

New ideas in the technical requirements in ISO/IEC 17025 that will likely be brought into NELAC Chapter 5 are:

- reference to "needs" of the clients;
- requirement for sampling plan when sampling done by laboratory;
- method validation;
- calculation/estimation of measurement uncertainty for testing laboratories; and
- provisions for inclusion of interpretations and opinions in test reports.

ISO/IEC 17025's management requirements also introduce some new aspects as compared to ISO/IEC Guide 25. Some new aspects found are:

- identification of potential conflicts of interest;
- more detailed requirements for quality policy statement;
- specific requirements for control, review, and approval, issue and amendment of documents;
- major changes in the Requests, Tenders and Contracts section (e.g., identify customer needs, ensure capability to meet needs, dealing with changes and deviations);
- incorporate ISO 9001 requirements in simplified form for purchasing;
- specific procedures for dealing with non-conforming work/results and the need for corrective action;
- specific procedures for cause analysis, selection and implementation of corrective action, subsequent monitoring and follow-up audits;
- preventive action requirements deals with potential problems and quality improvement process;
- records requirements now consistent with ISO 9001; and
- specific guidance on matter to be considered during management reviews.

Again, while the above are generally new aspects that will need to be considered, the overall ISO/IEC 17025 standard is much less prescriptive and introduces greater flexibility on how to accomplish the requirements. Some of the above items like corrective action, management reviews, records and reporting are already addressed in detail in NELAC Chapter 5. Actually the present NELAC Chapter 5 utilized some draft ISO/IEC 17025 language for the management reviews and corrective actions sections.

It is this inherent flexibility written into ISO/IEC 17025, especially in relation to method validation, that the PBMS Subcommittee hoped to capture in its draft section 5.10 and Appendix C language for Chapter 5 given below. Again the PBMS Straw Model elements/concepts are also based upon section 5.4 of the ISO/IEC 17025 standard. The following is the draft language for Chapter 5 section 5.10 that was presented at NELAC VII.

Please Note: This language is still draft and undergoing internal revisions by other PBMS Subcommittee members. It will be reviewed by the NELAC Quality Systems Committee. It is only being shared as part of this paper as a means to communicate the general direction the PBMS Subcommittee is heading with its extensive rewrite of section 5.10 and Appendix C. The revised 5.10 and Appendix C will be the keys to implementing ISO/IEC 17025 section 5.4 with the NELAC Quality Systems standards. I have been unable due to a limit on the size of the paper to include the draft work on other parts of Chapter 5 (e.g., Appendix C and D). I can be contacted at scott.siders@epa.state.il.us to request other sections (e.g., 5.9.4) or Appendices C and D.1 that are presently being worked by the PBMS Subcommittee.

Here, for your review, is the May 11, 2001, draft section 5.10 (pay special attention to 5.10.3) as drafted by the PBMS Subcommittee:

5.10 TEST METHODS AND STANDARD OPERATING PROCEDURES

5.10.1 Methods Documentation

a) The laboratory shall have documented SOPs on the use and operation of all equipment involved in the measurement, on the handling and preparation of samples and on calibration and/or testing, where the absence of such instructions could jeopardize the reliability of calibrations or tests.

b) All instructions, standards, manuals and reference data relevant to the work of the laboratory shall be maintained up-to-date and be readily available to the staff.

5.10.2 Laboratory Methods Manual and Standard Operating Procedures (SOPs)

The laboratory shall maintain a methods manual. The methods manual shall contain the laboratory's standard operating procedures (SOPs). The SOPs shall accurately reflect all phases of current laboratory activities such as sample receipt, sample storage, sample analysis, assessing data integrity, corrective actions, handling customer complaints, all test methods and data and record storage.

a) An SOP may be an equipment manual provided by a manufacturer, or an internally written document so long as the SOP is adequately detailed to permit someone other than the analyst to reproduce the procedures that had been used to produce a given result.

b) The test method SOPs may be copies of published methods as long as any changes or selected options in the methods are documented and included in the SOPs (see 5.10.1.2). Reference test methods that contain sufficient and concise information on how to perform the tests do not need to be supplemented or rewritten as internal procedures if these methods are written in a way that they can be used as published by the laboratory. It may be necessary to provide additional documentation for optional steps in the method or additional details.

c) Copies of all SOPs shall be accessible to all appropriate personnel.

d) SOPs shall be organized in a manner such that they are easily accessible to an auditor.

e) Each SOP shall clearly indicate its effective date, its revision number and shall bear the signature(s) of the approving authority.

f) Each test method SOP shall give or reference the following information, where applicable:

1.0 Scope and Application
2.0 Summary of Method
3.0 Definitions
4.0 Interferences
5.0 Safety
6.0 Equipment and Supplies
7.0 Reagents and Standards
8.0 Sample Collection, Preservation and Storage
9.0 Quality Control
10.0 Calibration and Standardization
11.0 Procedure
12.0 Data Analysis and Calculations
13.0 Method Performance
14.0 Pollution Prevention
15.0 Waste Management
16.0 References
17.0 Tables, Diagrams, Flowcharts and Validation Data

5.10.3 Use of Test Methods

All measurements made while operating as a NELAC accredited laboratory, must have an adequate demonstration that the measurement system provided data consistent with its intended use. The laboratory shall ensure the quality of results provided to clients by implementing a system to document the quality of the laboratory's analytical results. This demonstration consists of three activities: 1) an initial determination that the measurement system is capable of providing data of the quality needed to meet client and/or regulatory requirements (see 5.10.3.2), 2) an acceptable instrument calibration and verification that the system has remained calibrated during the period that it was used for analysis, and 3)

documentation of the quality of any data that was obtained. The specific activities performed for this demonstration are defined below and in Appendices C and D.

5.10.3.1 Method Selection

The laboratory shall utilize methods within its scope (including sample collection, sample handling, transport and storage, sample preparation and sample analysis) which are appropriate and applicable to client needs (i.e., to meet regulatory or other requirements specified by the client). These requirements may specify that a particular method, or group of methods, be employed for a given project or program, or that specific data or measurement quality objectives be achieved, or both, i.e., data or measurement quality objectives specified by the client or required of the client to demonstrate regulatory compliance define the boundary conditions of the method selection process.

a) When the use of a particular test method is mandated by a regulatory agency or is requested by a client, only that method shall be used. Deviations from a reference test method shall occur only if the deviation has been documented, technically justified, authorized and accepted by the client and/or regulatory agency. The laboratory shall inform the client when the method proposed by the client is considered to be inappropriate or out of date.

b) In the event that a specific method is not required by a regulation or a client, the laboratory may select another, alternative method, provided that it will yield data of sufficient quality to meet client requirements. When use of a particular method is not required by a client, the laboratory should preferentially employ methods published by consensus standards organizations, government agencies such as USEPA, reputable technical organizations or those that are published in peer reviewed journals. When using such a method, the laboratory shall ensure that it uses the latest valid edition of a method unless it is not appropriate or possible to do so. When necessary, the method shall be supplemented with additional details to ensure consistent application.

c) Laboratory-developed methods or methods adopted by the laboratory may also be used if not disallowed by state or federal regulation and are validated for the intended use. The client shall be informed as to the method chosen. If the selected method is changed, the validation shall be repeated.

d) Client approval of the methods to be used when conducting analyses must be obtained prior to implementation. Modifications must be documented in and referenced in reports to the client.

5.10.3.2 Method Evaluation

The laboratory must routinely evaluate and document the quality of the measurement system relative to the materials being tested. This activity is termed “method evaluation.” The thoroughness and robustness of the evaluation depends on what is already known about the performance of the method on the analyte-matrix combination of concern over the concentration range of interest. Properties of the measurement system to be evaluated include bias, precision, sensitivity and selectivity. The measurement system includes the analyst (operator) or work cell and method.

Essential elements of method evaluation include measures to determine positive or negative bias, to assess variability and/or repeatability, to determine sensitivity, range and response, to ensure selectivity of the test method for its intended purpose and to ensure constant and consistent test conditions where required by the system.

The laboratory shall evaluate each method for its intended use according to Appendix C. The laboratory shall record the results of the evaluation, the protocol used for the evaluation and the basis for the stated measurement system performance. When changes are made in a method, the influence of such changes shall be documented and, if appropriate, a new evaluation shall be carried out.

The thoroughness of any method evaluation is always a balance between costs, technical possibilities, available time and the consequences of error. There are many cases in which the range and uncertainty of the values (e. g. accuracy, detection limit, selectivity, linearity, repeatability, reproducibility, robustness and cross-sensitivity) can only be approximated. However, so long as the level of approximation is commensurate with the needs of the client, such tradeoffs are acceptable.

5.10.3.3 Quality Control Procedures

In addition to the requirement for evaluation, the following general quality control procedures shall apply, wherever applicable. The manner in which they are implemented is dependent on the types of tests performed by the laboratory (i.e., chemical, whole effluent toxicity, microbiological, radiological, air) and are further described in Appendix D. The standards for any given test type shall assure that the applicable principles are addressed.

a) The laboratory shall have quality control procedures in place to monitor the performance of the measurement system on an on-going basis, including:

    1) procedures to ensure that the measurement system is free of laboratory induced interferences;

    2) procedures to identify if and when analytical instruments are in an out-of-control condition;

    3) procedures to verify continuing analyst proficiency;

    4) procedures to ensure the suitability of reagents and standards; and

    5) measures such as temperature, humidity, light or specific instrumental conditions, to assure constant and consistent test conditions (both instrumental and environmental) where required by the test method.

b) All quality control measures shall be assessed and evaluated on an on-going basis, and quality control acceptance criteria shall be used to determine the usability of the data. (See Appendix D.)

c) The laboratory shall have procedures for the development of accept/reject criteria where no method or regulatory criteria exist. (See 5.11.2, Sample Acceptance Policy.)

The essential quality control measures for testing are found in Appendix D of this Chapter.

SUMMARY

As you can imagine Appendix C will be integral in regards to the method validation step. I want to reiterate that the above is only an internal draft still subject to change and did not represent proposed language up for vote at NELAC VII. I hope sharing this draft language helps foster discussion and disseminates information on the NELAC Quality System Committee's present efforts.

Again, the advent of ISO/IEC 17025 and the PBMS Straw Model are generating considerable discussion and efforts within the NELAC Quality Systems Committee and its PBMS Subcommittee. This paper is an attempt to capture the direction the Committee is heading to address these items as they relate to quality systems. It is the hope of the NELAC Quality Systems Committee to present at the next NELAC Interim Meeting (NELAC VIII) a complete document that will highlight possible proposed language. Prior to NELAC VIII the Quality Systems Committee and the PBMS Subcommittee will welcome your feedback on the direction they are taking. The USEPA, DOD, other federal agencies, States and the private sector are significant stakeholders in this process and need to participate fully in NELAC to ensure the quality systems standards developed do indeed improve overall data quality.

Special thanks to the members of the NELAC Quality Systems Committee, PBMS Subcommittee and the ISO/IEC 17025 Subcommittee whose members come from states, federal agencies and the private sector. This work is being done by good people in a true spirit of partnership.

THE TECHNICAL ASPECTS OF THE NELAC PROFICIENCY TESTING PROGRAM

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The National Environmental Laboratory Accreditation Conference (NELAC) Proficiency Testing (PT) Program is an important tool in the NELAC accreditation process. The goals of the PT program are the generation of data that meets the needs of environmental and regulatory programs, as well as the improvement of the overall performance of laboratories. The PT standards were constructed to meet these goals and the NELAC PT Committee has expanded the standards to be more inclusive and improved the standards as needs were identified.

The PT program evaluates a laboratory's performance under controlled conditions relative to a given set of criteria. NELAC PT samples are unknown samples provided by an external source. There were major changes in the PT program at the time of the onset of NELAC. Many more National Environmental Laboratory Accreditation Program (NELAP) Accrediting Authorities expanded the range of needed PT samples. Coincidently, the EPA PT program for drinking water and non-potable water was privatized. As a result, multiple PT providers are now servicing the NELAC community, which introduced complexities not previously existent. The PT Committee responded by developing standards to assure that 1) the samples provide an equivalent challenge to laboratories regardless of which PT provider is used and 2) uniform pass/fail criteria are used by all PT providers.

With the recognition of eleven states as NELAP AAs, the PT program became operational when these states began accepting applications for NELAC accreditation in 1999. The program is successful but is constantly being modified as new issues rise to the surface. Several key issues currently being addressed include 1) evaluation and expansion of the PT field of testing, 2) evaluation of acceptance criteria, 3) standardization of method codes, analyte codes and report format, 4) use of PT samples for corrective action purposes and 5) oversight of PT providers.

STATUS OF RCRA INORGANIC METHODS PROGRAM

B. Lesnik
U.S. EPA

No abstract available.

ANALYSIS OF ENVIRONMENTAL SAMPLES BY ICP-MS USING DYNAMIC REACTION CELL TECHNOLOGY TO ELIMINATE INTERFERENCES

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ABSTRACT

There is much confusion regarding the differences between the various types of “cell-based” ICP-MS instruments that are currently available. This paper discusses these differences based on the device placed inside the reaction cell. The device can either be a mass-filtering device such as an active quadrupole or a passive multipole ion guide device. In the passive ion guide systems, the multipole (usually a hexapole or an octopole) is not utilized as a mass filter, but rather an ion-focusing device. This paper will show the advantages of using an active mass filter inside the reaction device to precisely control the chemistry occurring and present data illustrating the usefulness of the ELAN® Dynamic Reaction Cell™ (DRC™) ICP-MS with Dynamic Bandpass Tuning (DBT) capabilities for environmental analyses.

INTRODUCTION

ICP-MS has now been available commercially for over 15 years. The technique has gained wide acceptance with the majority of the environmental testing community due to its speed and sensitivity, replacing graphite furnace atomic absorption spectrometry in many laboratories. Many countries, the USA included, now have routine ICP-MS methods for the analysis of trace elements in environmental samples (see Table 1). The trend toward lower maximum contaminant levels in drinking waters and soils, as well as the increasing interest in speciation analysis will continue to make ICP-MS a valuable tool for the environmental laboratory.

Table 1. Regulatory limits for drinking water from USA, Germany, UK and Japan.

	UK	Germany	USA	Japan
Element	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Ag	0.010	0.010	0.100	0.100
Al	0.200	0.200	0.200	
As	0.050	0.010	0.05/0.01	0.010
B	2.000	1.000		1.000
Ba	1.000	1.000	2.000	
Be			0.004	
Ca	250			
Cd	0.005	0.005	0.005	0.010
Cr	0.050	0.050	0.100	0.050
Cu	3.0	3.0	1.0	1.0
Fe	0.200	0.200	0.300	0.300
Hg	0.001	0.001	0.002	
K	12	12		
Mg	50	50		
Mn	0.001	0.050	0.050	0.050
Mo	0.010			0.070
Na	0.500	150.000		
Ni	0.004	0.050		0.010
P	0.037	5.000		
Pb	0.003	0.040		0.050
Pt	0.020			
Sb	0.000	0.010	0.006	0.002
Se	0.000	0.010	0.050	0.010
Si	0.068			
Sn	0.050			
Sr	0.010			
Tl	0.010		0.002	
V	0.002			
Zn	0.016	5.000	5.000	1.000
U			0.030	0.002

However, since ICP-MS was developed in the early 1980s it has experienced limitations when applied to the determination of several key elements in certain types of environmental sample matrices. Some examples of interferences that are common in environmental samples are given in Table 2. The effect of these interferences is to limit the ability to detect and accurately determine low levels of these elements in the target matrix.

Table 2. Common interferences in ICP-MS, the elements affected by them and most common environmental samples where they are found.

Interfering Species	Elements Affected	Typical Matrix
$^{40}Ar^{35}Cl$, $^{40}Ar^{37}Cl$	^{75}As, ^{77}Se	3050-ICP, brines, seawaters
$^{35}Cl^{16}O$, $^{37}Cl^{16}O$	^{53}Cr	3050-ICP, brines, seawaters
$^{40}Ar^{12}C$	^{52}Cr	TCLP, organics
$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	^{56}Fe	Wastewaters – CaO processed
$^{40}Ca^{18}O$, $^{44}Ca^{16}O$	^{58}Ni, ^{60}Ni	Wastewaters – CaO processed
$^{40}Ar^{23}Na$	^{63}Cu	Brines, seawater

The development of ICP-MS instruments with gas-filled cells between the plasma and the analyzer quadrupole has shown great promise in reducing polyatomic interferences. However, these instruments do have limitations and it is important to understand what they are, how they may affect an analysis and what the differences are between the two types of "cell-based" ICP-MS systems.

Cell-based ICP-MS instruments can be categorized into two classes, depending on the configuration and operating conditions of the cell. The first type of cell system that was developed was the collision cell system. These systems evolved from the collision cells that were developed in the early 1980s for organic mass spectrometry (e.g., LC-MS systems). The first commercial collision-cell ICP-MS was introduced in 1987. In a typical collision cell system, a multipole is placed inside an enclosed cell located in the ion path of the instrument. The purpose of the multipole is to keep all the ions focused inside the cell and to funnel them into the analyzer quadrupole – in other words, it acts as an ion guide. The multipole used is typically a hexapole or octopole, as these devices are more efficient as ion focusing devices. In fact, in many designs the multipole collision device actually replaces part of the normal ion lens assembly of a typical non-cell system. Because this type of collision cell system uses a passive (or non-mass filtering) ion-guide in the cell, we can also refer to these systems as passive ion-guide systems in order to avoid further confusion.

Passive ion-guide collision systems typically rely on collisional induced dissociation (CID) caused by the collision of the reaction gas molecules with the analyte and inteferent ions inside the cell to reduce some common polyatomic interferences. Typically, collision cells operate under lower pressures and higher ion energies than reaction cells. Because collision cells operate at higher ion energies, some endothermic reactions (i.e. reactions that require energy input) may occur, but these reactions are secondary and are not predictable or controllable[1,2]. Another point to note is that although the collision cell instruments commercially available for ICP-MS operate at fairly high gas flow rates, this is due to the design of the collision cell and does not indicate the actual pressure inside the cell. In a passive ion-guide system, the only way to attempt to control the collisions and reactions that may occur is to limit the total number of gas molecules present for collision by keeping the pressure in the cell low and limiting the gases used to those that are fairly non-reactive, such as hydrogen or helium.

The second type of system is a dynamic reaction cell system. Currently only one dynamic reaction cell system is available, the ELAN Dynamic Reaction Cell or DRC. The ELAN DRC has been available commercially since early 1999. A dynamic reaction cell system is one where an active mass-filtering device is placed inside the reaction cell. In the case of the ELAN DRC, an active quadrupole is used inside the cell and is controlled to act as a mass filter. The ELAN DRC eliminates interferences through two mechanisms: chemical resolution and Dynamic Bandpass Tuning (DBT). Chemical resolution uses the **chemical reactions** between the interfering species and the reaction gas to create products that do not interfere with the analyte of interest. The chemical reactions occurring inside the dynamic reaction cell are between ions that are essentially at thermodynamic equilibrium (also called thermalized ions[2-5]). In order to have ions that are thermalized inside a reaction cell, the pressure inside the cell must be relatively high and the energy of the ions relatively low. This results in only predictable exothermic reactions taking place within the cell. As a result, in the ELAN DRC, the chemistry (and it is ***chemistry*** that occurs, not just collisions) is predictable using gas-phase kinetic and thermodynamic theory and is transferable from instrument to instrument. This is not the case with passive ion-guide collision cell systems, and significant performance variations have been reported from one instrument to another.

Dynamic Bandpass Tuning (DBT) uses the application of a precisely controlled bandpass mass filter inside the dynamic reaction cell to exclude and eject undesirable species from the reaction cell, preventing the formation of new interferences. The use of an active quadrupole inside the dynamic reaction cell allows a mass bandpass window with both low-mass and high-mass cutoff regions to be established. This mass bandpass window is tunable and changes appropriately with the analyte mass being passed through to the analyzer quadrupole – hence the term Dynamic Bandpass Tuning or DBT. Because product ions can be expelled from the reaction cell, highly reactive gases, such as ammonia, oxygen, methane and others can be used.

The major difference between the active quadrupole used in the ELAN DRC and the passive ion-guide configurations is their ability to deal with the formation of new species created within the cell. The passive ion-guide systems do not have the ability to establish a precise mass bandpass window inside the cell. In fact, these devices are designed purely to transmit *all* of the ions that are within the cell to the analyzer quadrupole. As a result, most ions (collision products as well as matrix ions) are stable within the collision cell, providing an opportunity for unwanted and uncontrollable reactions and collisions to occur. This leads to the formation of new interferences and causes higher signal backgrounds. Although this is especially true when using highly reactive gases such as ammonia, even simple gases will produce new interferences from the uncontrolled chemistry inside a passive ion-guide collision cell. These new interferences may obscure masses that have traditionally been interference-free in ICP-MS. There have even been reports at recent conferences by users of these systems that the reactions that are occurring are due to impurities in the reaction gas. Because these simple collision cell instruments do not have any means of controlling the collisions/reactions that occur inside the cell, they must limit the use of gases to simple gases, such as H_2 or He, which limits somewhat the possibility of additional interferences being formed. However, this results in a great compromise and non-ideal operation because these gases are less effective in the removal of the primary interference, particularly under the conditions used in the passive ion-guide systems. In addition, the passive ion-guide systems must limit the number

of reactions/collisions that occur to just a few by maintaining a low pressure inside the cell, otherwise, the rate of formation of new interferences is too high and the resulting analyte signal loss is too great.

The advantage of the ELAN DRC is that the quadrupole inside the cell has well-defined stability regions, which can be easily controlled by the application of the RPq and RPa parameters to adjust the low- and high-mass cutoff regions, thus establishing the DBT parameters. This means that ions outside the low- and high-mass stability boundaries are unstable in the cell and are ejected. The bandpass sets up an electric barrier that allows interferences to leave the analyte stability region, but does not allow any new interferences (from recombination, for example) to enter. This provides an excellent means of completely controlling the chemistry that occurs inside the DRC beyond simply changing the reaction gas used and gas flow rate. Another advantage of the ELAN DRC is its ability to filter out these unwanted ions so that they have no possibility of reacting to form new ions that might interfere with masses of interest. This means that the reactions eliminating the interfering species can be allowed to continue to completion, efficiently removing the interference, not just reducing it. In contrast, passive ion-guide systems using kinetic energy discrimination can never allow the reactions to go to completion; otherwise they lose analyte sensitivity[2]. This is why the level of interference reduction reported on an active quadrupole system like the ELAN DRC can be between 1,000-1,000,000 times better than that of passive ion-guide systems[2,6].

By using patented Dynamic Reaction Cell technology, the interferences shown in Table 2 can be eliminated though the use of chemical resolution and dynamic bandpass tuning. The DRC ICP-MS uses an active quadrupole inside the cell to establish a mass bandpass and provide complete control over the chemistry occurring inside the cell. This provides an excellent means of controlling the desirable and undesirable product ions that occur inside the cell, no matter what type of reaction gas is used or sample matrix is present.

In contrast, cell-based systems that use passive ion guide technology have no way of controlling the chemistry occurring inside the cell. These systems generally rely on post-cell energy filtering to distinguish between the analyte- and cell-based ions, limiting their applicability to real sample matrices. Since passive ion guide systems are designed to transmit all of the ions entering the cell to the analyzer quadrupole, the large number of matrix ions from complex samples can create additional interferences.

Real sample matrices from environmental sites are generally complex and their exact makeup is usually unknown and unpredictable. As a result, the ability to control the chemistry occurring inside the cell becomes extremely important when a cell-based system is used for analytical determinations. In addition, a single gas may not give the best performance in all samples for all analytes, as would be expected from themodynamic calculations.

The results of experiments performed on an ELAN DRC*Plus* using typical “collision cell” conditions where the dynamic bandpass tuning parameters were essentially turned off to mimic what would happen in a typical passive ion guide system are shown in Figures 1a-1d, which display four spectra of 10 µg/L zinc, acquired using ammonia as a reaction gas (flow rate = 0.70 mL/min) at two different RPq or bandpass settings. An RPq setting of 0.25 was used to simulate the conditions inside a passive ion-guide collision cell system while an RPq

setting of 0.65 was used as the optimized DBT setting on the ELAN DRC. At RPq=0.25 (dashed-black spectrum), $Zn(NH_3)_x$ (x=1-3) clusters form due to reactions within the reaction cell of species from both the reaction gas and the sample matrix. The presence of these clusters obscures the determination of analytes that may be present at these masses, such as Sr, Mo and Sn, as seen in Figures 1b-1d. However, by increasing RPq to 0.65 (solid-blue spectrum) in the DRC, the formation of $Zn(NH_3)_x$ cluster ions does not occur and the trace amounts of Sr and Sn present in the sample can now be seen. This example demonstrates that the dynamic bandpass tuning capabilities of the DRC prevent the formation of new, interfering species within the cell by allowing complete control over the chemistry occurring inside the cell. In contrast, other cell-based systems do not have the ability to apply a mass bandpass inside the cell. As a result, ions from both the reaction gas and more importantly, the sample matrix can react to form new interferences. This greatly limits the ability of other cell-based systems to remove interferences in real world sample matrices.

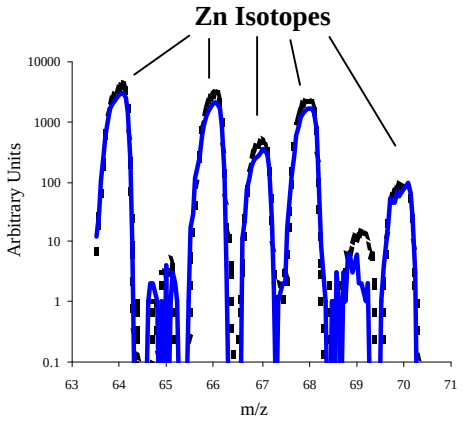

Figure 1a.

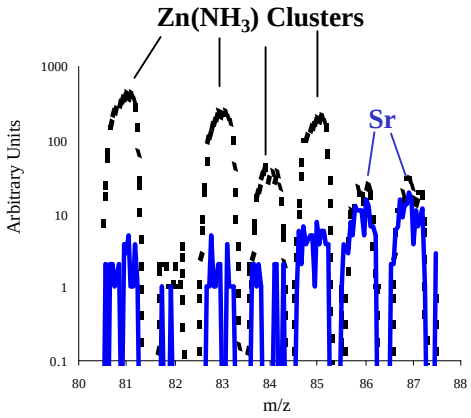

Figure 1b.

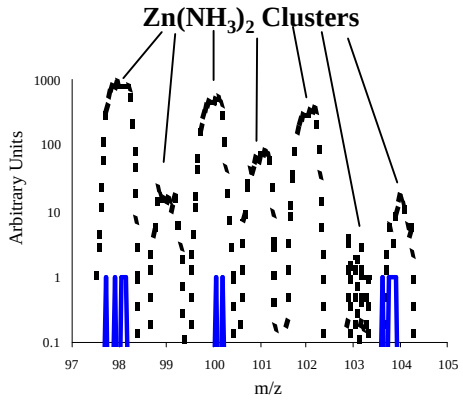

Figure 1c.

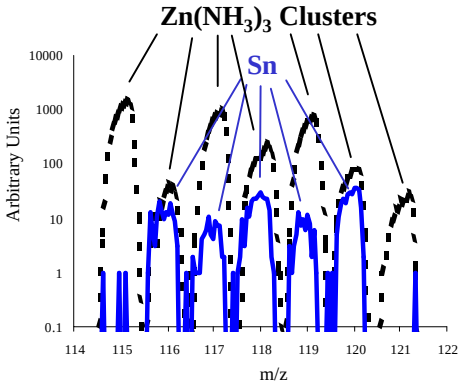

Figure 1d.

Figures 1a-1d. Spectra of 10 ppb zinc with RPq=0.25 (dashed-black spectrum) and RPq=0.65 (solid-blue spectrum). Sr and Sn are present in trace amounts. Figure 1a shows the Zn peaks from masses 64 to 68. Figure 1b shows the mass region from 80-87. Figure 1c shows the mass region from 97-105. Figure 1d shows the mass region from 114-121. Figures 1b, 1c and 1d illustrate the $Zn(NH_3)_x$ clusters (dashed-black spectrum) that can form without the ability to establish a mass bandpass window inside the reaction cell.

RESULTS

Much work has been done on the ELAN DRC*Plus* to determine the best reaction gases and conditions to obtain the ultimate detection limits for many elements in various matrices, from environmental samples to semiconductor grade chemicals. Knowing that most production environmental laboratories do not require the best possible detection limits in every sample matrix nor do they have the time to run each sample separately for each element, a universal method was developed for environmental analyses. This universal method used a single gas, ammonia and a single reaction gas flow rate for six elements run in DRC mode (Al, V, Cr, Fe, As and Se). The DBT conditions were optimized to provide the best possible results for these target elements in the sample at the same time. Other elements from US EPA Method 200.8 were run in the same method, using normal mode (non-DRC) conditions. This method was then used to perform detection limit studies and to analyze several samples. The results and detection limits obtained using the universal method (see Table 3) under normal mode were similar to those obtained on the ELAN 6100. Table 4 compares the IDLs obtained for the

elements also determined in DRC mode using the universal method with the IDLs obtained in both normal mode and those obtained in DRC mode with full optimization of the reaction gas and gas flow rate for the best possible detection limit. As expected, the detection limits obtained with the universal environmental method were inbetween those of conventional ICP-MS (normal mode) and the fully optimized DRC mode. In addition, overall stability over a 5-hour analytical run was similar to that seen on a conventional ELAN 6100 ICP-MS instrument (see Figure 2).

Table 3. IDLs obtained using the universal environmental method on the ELAN DRC*Plus* for elements determined in normal (non-DRC) mode.

Element	Mass	IDL (µg/L)	MDL (µg/L)
Be	9.00	0.01	0.02
B	11.00	0.24	0.22
Mn	55.00	0.02	0.05
Co	59.00	0.002	0.002
Ni	60.00	0.004	0.004
Cu	63.00	0.004	0.004
Zn	66.00	0.02	0.02
Mo	98.00	0.004	0.003
Ag	107.00	0.001	0.002
Cd	114.00	0.05	0.01
Ba	135.00	0.02	0.12
Hg	202.00	0.02	0.02
Tl	205.00	0.004	0.002
Pb	208.00	0.02	0.01
Na	23.00	0.20	0.10
Mg	24.00	0.007	0.04
K	39.00	1.30	3.40
Ca	44.00	2.70	4.60

Table 4. Comparison of universal environmental method DRC-mode detection limits with normal mode detection limits and optimized DRC-mode detection limits.

Element	Mass	Normal Mode IDL (µg/L)	Universal Method DRC mode IDL (µg/L)	Optimized DRC Mode IDL (µg/L)
Al	27.00	0.037	0.029	0.0002 (c)
V	51.00	0.012	0.003	0.00012 (c)
Cr	52.00	0.027	0.001	0.0002 (c)
Fe	56.00	0.760	0.012	0.0003 (c)
As	75, 91	0.012, na	0.039, 0.083	0.0006 (75)
Se	78, 82	na, 0.11	0.055, 0.026	0.0012, 0.0007(80)

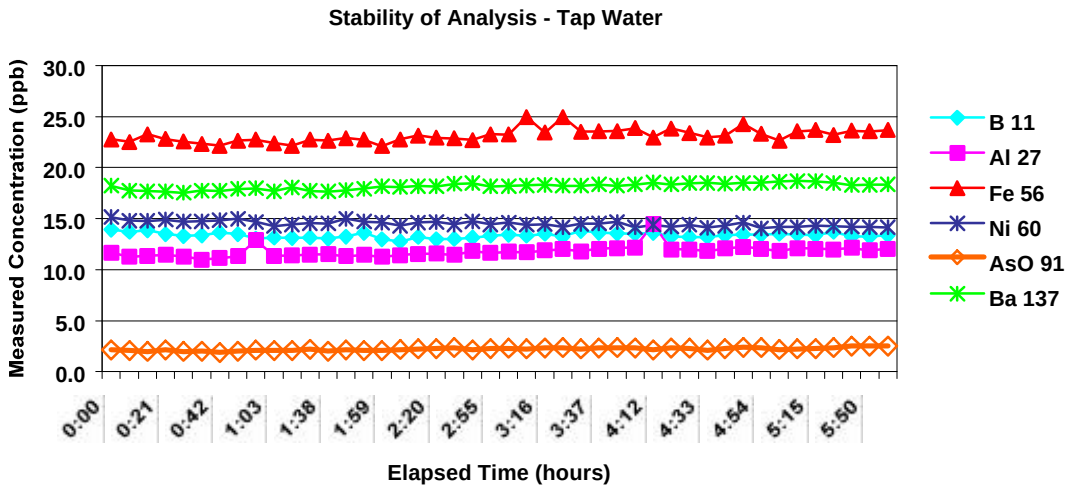

Figure 4. Stability of ELAN DRC*Plus* for elements determined in tap water in both normal and DRC modes using the universal environmental method over a period just under 6 hours.

SUMMARY

The data presented here illustrate that the ability to establish low- and high-mass bandpass windows on a cell-based ICP-MS system like the ELAN DRC*Plus* eliminates the possible formation of new interferences is an important capability for the analysis of real sample matrices, which may vary greatly in their overall matrix content. The study also shows that a single universal environmental method combining both normal and DRC modes of analysis can be used to determine all the elements required in US EPA Method 200.8. For elements that may be affected by common polyatomic interferences, the use of DRC mode will allow better detection limits in a wide variety of matrices, by eliminating the interferences. Similar stability to conventional ICP-MS was obtained over a period of nearly six hours. If better detection limits are required for some elements than those obtained using the universal method in DRC mode, these can be obtained by running them under completely optimized reaction gas and gas flow conditions. This can be done in the same method as the other non-DRC and DRC elements, with some increased analysis time.

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SPECIATION OF MERCURY IN SOIL AND SEDIMENT BY SELECTIVE SOLVENT AND ACID EXTRACTION, DRAFT METHOD 3200

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No abstract available.

CHARACTERIZING PM-2.5 EMISSIONS FROM SPECIFIC SOURCE CATEGORIES

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Abstract

In July, 1997, the U.S. Environmental Protection Agency (EPA) promulgated a new National Ambient Air Quality Standard (NAAQS) for ambient particulate matter (PM) of aerodynamic diameter 2.5 µm or less (PM-2.5) and revised the existing standard for ambient particles of aerodynamic diameter 10 µm or less (PM-10). Implementation of the new standard has been delayed to allow EPA time to better understand the factors underlying the observed correlation between ambient fine particulate matter and adverse human health effects and to better evaluate risk management options. To support development of this better understanding, the Emissions Characterization and Prevention Branch (ECPB) of the EPA Air Pollution Prevention and Control Division (APPCD) is conducting research to characterize PM-2.5 emissions from specific source categories in order to update and improve source emission profiles and emission rates for PM-2.5 with the dual aim of improving the quality of data used for dispersion and receptor modeling of ambient PM-2.5 and of providing quality emissions data for evaluation of risk management strategies. To obtain collected PM representative of the PM collected by ambient monitors downstream of the source, PM samples were collected to simulate the processes of cooling, condensation and mixing that occur when material leaves a stack as hot exhaust gas.

The first of several planned field tests was conducted at a wood-fired industrial boiler equipped with an electrostatic precipitator control device to evaluate the sampling equipment and to characterize the fine particulate emissions. To simulate the behavior of fine particles as they enter the ambient atmosphere from an emissions source, dilution sampling was performed to cool, dilute and collect gaseous and fine particulate emissions from a wood-fired industrial boiler. Gaseous and fine particulate material collected during the sampling was also characterized. ERG coordinated all field test activities; laboratory testing activities were divided between EPA and ERG. ERG performed source sampling to collect artifact-free, size-resolved particulate matter in a quantity and form sufficient to identify trace elements and organic compounds and to distinguish gas-phase and particle-phase organic compounds. Total particulate matter mass in the diluted and cooled emissions gas was size-resolved at the PM-10 and PM-2.5 cut points with the PM-2.5 fraction further continuously resolved down to 30 nm diameter using a scanning particle mobility analyzer. Emission factors were calculated for the source, using the micrograms of material collected and the mass of fuel consumed during the sampling period.

Introduction

The mission of the ECPB of the APPCD/EPA is to characterize source emissions and develop and evaluate ways to prevent those emissions. Source characterization as defined here

includes the measurement of PM mass emission rates, source PM profiles (PM chemical composition and associated chemical mass emission rates) and emission rates of ambient aerosol precursors such as SO_x, NO_x and NH_3. The overall objective of this program is to update and improve source emission profiles and emission rates for PM-2.5 with the dual aim of improving the quality of data used for dispersion and receptor modeling of ambient PM-2.5 and of providing quality emissions data for evaluation of risk management strategies. Source types for testing in this program were selected on the basis of the quantity of fine PM emitted by the source type as determined from emission inventories and on the basis of the quality of existing PM-2.5 source profiles for each source type. Dilution sampling was used to simulate the processes of cooling, condensation and mixing that occur when material leaves a stack as hot exhaust gas and is cooled by interaction with ambient air.

Dilution Sampling System

The dilution sampling system used in the source test was based on the original design by Dr. L. M. Hildemann (Hildemann, 1989), modified to incorporate more secure closure fittings and electronic controls. Automatic flow control and data acquisition capabilities were added to the dilution sampler to improve the ease of operation of the unit. A touchscreen interface connected to the main controller was used to monitor current conditions and allow setpoints to be entered into the system readily. A laptop computer was used for continuous monitoring of operating parameters and logging of process data.

ECPB/EPA built a state-of-the-art dilution sampler to deploy in the performance of this field testing effort. The dilution sampling system dilutes hot exhaust emissions with clean air to simulate atmospheric mixing and particle formation. Control of residence time, temperature and pressure allows condensible organic compounds to adsorb to fine particles as they might in ambient air. The sampler is also designed and fabricated to minimize any contamination of samples, especially organic compound contamination, and to have particle losses to the sampler walls of no more than approximately 7 percent.

A clean air system provides High Efficiency Particulate Arresting (HEPA) and carbon-filtered air for dilution of source emissions. Acid gases (if present) will not be removed completely by the dilution air conditioning system, but the presence of acid gases can be monitored in the dilution tunnel immediately downstream of the dilution air inlet. The dilution air conditioning system can be modified to add a heater, a cooler and dehumidifier, as needed. Cleaned dilution air enters the main body of the sampler downstream of the dilution air orifice meter, as shown in Figure 1. The key zones of the dilution sampling system and their function are described below.

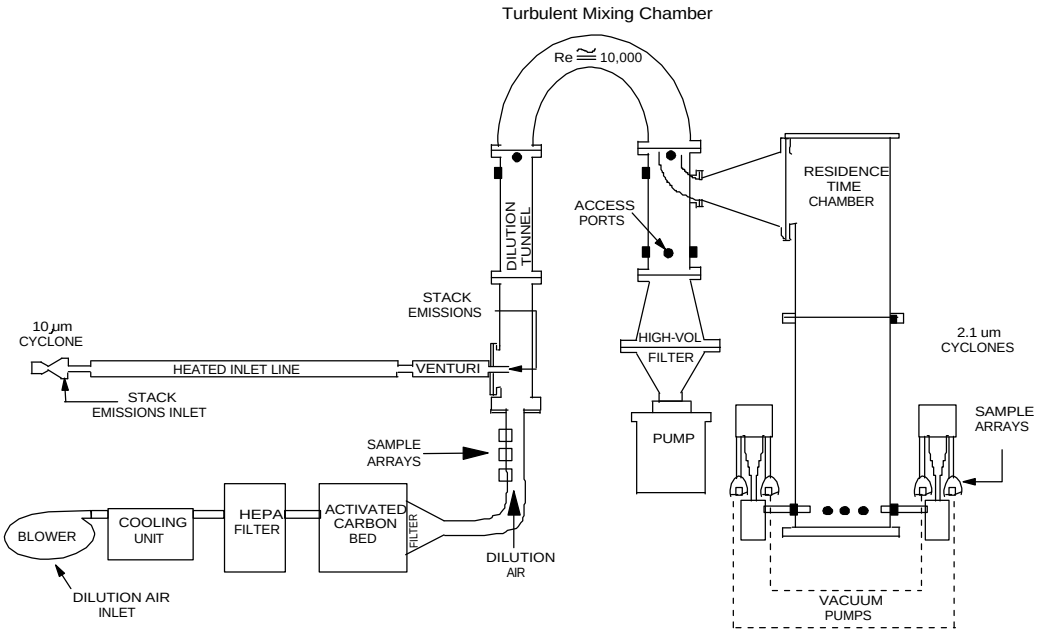

Figure 1

Sample Inlet Zone –
Stack Emissions Inlet: designed to allow source exhaust gas to be sampled through an inlet cyclone separator to remove particles with nominal aerodynamic diameters > 10 µm. The PM-10 cyclone prevents large particles from entering the sampler to plug or damage the equipment. Three ports are available for sampling the dilution air before it mixes with the source gas.

Heated Inlet Probe: 3/4" heated stainless steel sampling probe draws source gas through a venturi meter into the main body of the sampler. Sample flow rate can be adjusted from 15-50 Lpm (typically 30-40 Lpm).

Venturi Meter –
Constructed of low carbon, very highly corrosion-resistant stainless steel; equipped for temperature and pressure measurement. Wrapped with heating coils and insulated to maintain the same isothermal temperature as the inlet cyclone and inlet line.

Turbulent Mixing Chamber –
Consists of an Entrance Zone, U-Bend and Exit Zone. The inside diameter is 6 in., yielding a Reynolds number of ~10,000 at a flow rate of 1000 Lpm. Dilution air enters the Mixing Chamber in a direction parallel to the flow of source gas. Hot source gas enters the Chamber perpendicular to the dilution air flow, 4.5 in. downstream of the dilution air inlet. The combined flow travels 38 in. before entering the U-Bend. After the Residence Chamber Transfer Line, the Mixing Chamber continues for 18 in., then expands to an in-line high-volume sampler filter holder. Collected particulate has not experienced time to equilibrate with the gas phase at the diluted condition. Sample and instrumentation ports are installed on the Turbulent Mixing

Chamber at various locations.

Residence Time Chamber –
The Inlet Line to the Residence Time Chamber expands from a 2 in. line (sized to provide a quasi-isokinetic transfer of sample gas from the Turbulent Mixing Chamber to the Residence Time Chamber at a flow rate of ~100 Lpm) within the Mixing Chamber to a 7 in. line at the wall of the Residence Chamber. The flow rate is controlled by the total sample withdrawal from the bottom of the Residence Time Chamber and provides a 60-sec. residence time in the Chamber. Twelve ports are installed at the base of the Residence Time Chamber: nine ports for sample withdrawal and three ports for instrumentation.

Sample Collection Zone –
Samples collected from the sample ports at the base of the Residence Time Chamber have experienced adequate residence time for the semivolatile organic compounds to re-partition between the gas phase and the particle phase.

For the test conducted on August 8-9, 2000, the calculated total time the sample spent in the dilution sampling system was 73 seconds: 2.4 seconds for the Turbulent Mixing Chamber and 70.6 seconds for the Residence Chamber.

Sample Collection Arrays
Virtually any ambient sampling equipment (including filters, denuders, PUF cartridges, DNPH-impregnated sampling cartridges, SUMMA®-polished canisters, cyclones, particle size distribution measurement instrumentation) can be employed with the dilution sampling system. The exact number and type of sample collection arrays is uniquely configured for each testing episode. Dilution Chamber Ports used PM-2.5 cyclones branching off to quartz filters backed by PUF, Teflon® filters backed by KOH-impregnated quartz filter, and a Teflon® filter before a SUMMA® canister. Residence Chamber sampling ports used PM-2.5 cyclones leading to parallel Teflon® filters, to parallel quartz filter/PUF plug assemblies, and to parallel Teflon® filter assemblies followed by KOH-impregnated quartz filters, as well as to a set of two 200 mm long XAD-4®-coated denuders in series followed by two parallel quartz filters both leading into PUF sampling modules. Additional sampling ports at the Residence Chamber were used to sample SUMMA® canisters, DNPH-impregnated silica gel tubes and an aerodynamic particle-sizing spectrometer. Samples projected for collection are shown in Table 1.

Table 1. Sampling Media Used for Collection of Samples, Analysis Performed, Analytical Method and Responsible Laboratory

Sampling Medium	Analysis	Method	Responsible Laboratory
Teflon® Filter	PM-2.5 mass	Gravimetric (GRAV)	EPA
Teflon® Filter	Elemental Analysis	X-ray fluorescence (XRF)	EPA
Teflon® Filter	Inorganic Ions	Ion Chromatography (IC)	EPA
Quartz Filter	Elemental Carbon/Organic Carbon	Thermal-Optical Evolution (TOE)	EPA
Quartz Filter XAD-4® Denuder PUF	Organic species	Gas Chromatography/Mass Spectrometry (GC/MS)	EPA
DNPH-impregnated silica gel tubes	Carbonyl compounds	High Performance Liquid Chromatography (HPLC, Method TO-11A)	ERG
SUMMA® canisters	Air Toxics Speciated Nonmethane Organic Compounds (NMOC)	GC/MS Method TO-15 ERG Concurrent Analysis	ERG
Particle Size Analyzer	Particle size distribution	Ion mobility spectrometer	ERG

Site Operation/Process Description

An industrial wood/bark waste-fired boiler was selected as the test site. The boiler was a relatively modern field-erected watertube pneumatic vibrating stoker-type unit designed and erected by Steam & Control Systems, Inc. When operating at the designed heat unit input rate, the boiler generates 165,000 lb of steam per hour of continuous 960 psig/760ºF superheated steam. The boiler utilized wood as the primary fuel and natural gas as start-up and backup fuel. The combustion unit was a pyrolysis system designed to gasify wood in the initial combustion zone at sub-stoichiometric air rates. The initial combustion zone is on the grate; complete combustion of the off-gases from the pyrolysis process occurs in a secondary combustion zone located above the initial combustion zone. Emissions are controlled by a multicyclone-type dust collector, followed by a multi-stage electrostatic precipitator.

The boiler was operated with a continuous screw-feed conveyor belt, with continuous weighing of the wood chips fed to the boiler. The test series was scheduled to minimize disruption to the normal operation of the test facility and to enable as much simultaneous data collection important to all parties as possible. Boiler fuel consisted of chipped municipal and residential yard waste wood – i.e., branches, limbs, twigs, tree trunks, stumps or roots that had passed through a chipper/shredder and was delivered to the test site via dump truck for storage until use. The facility utilized a large outdoor storage wood pile that was approximately 800 ft long, 800 ft wide and 60 ft deep. While the test team was on site, two samples of wood chips that were composited from all over the wood pile were collected for subsequent analysis, as shown in Table 2.

Table 2. Analytical Results from Wood Chips

Parameter	As Received, %	Dry Basis, %
Moisture	38.9	N/A*
Volatile Matter	52.67	86.2
Fixed Carbon	7.38	12.08
Ash	1.05	1.72
Sulfur	0.01	0.02
Carbon	30.85	50.5
Hydrogen	3.55	5.81
Nitrogen	0.15	0.25
Oxygen	25.49	41.69
BTU/lb	5537	9062

*Not applicable.

Pre-Test Survey

A thorough survey of the test site was performed to determine that the test equipment could fit in the test location and to identify and gain access to the utilities needed to operate the dilution system and its ancillary equipment, to arrange for installation of sample collection ports at the outlet of the ESP and to determine the means of positioning the sampler at the desired location. The sampling location was a flat metal deck (approximately 50 ft x 50 ft) on top of the ESP scrubbing system, approximately 60 ft above ground level. The two modules required for sampling were positioned at the sampling location using a crane supplied and operated by the facility.

Field Test

EPA Methods 1-4 were used to establish traverse points, determine volumetric flow rate, calculate flue gas velocity, measure O_2 and CO_2, determine stationary gas distribution, dry molecular weight of flue gas, wet molecular weight of flue gas, average moisture, volume of dry gas sampled at standard conditions and dry mole fraction of flue gas. A pre-test leak check and orifice flow check were performed. A pre-test was performed prior to the initiation of source testing to establish the length of the integration period for the test runs so that the substrate loading could be estimated in order to avoid overloading the substrates during the actual testing. Actual testing at the site was conducted on August 8 and 9, 2000. Testing was performed for 258 minutes on August 8; 360 minutes on August 9. The sample collection modules were recovered in the field at the end of the respective runs and transported to the Research Triangle Park laboratories for the analyses shown in Table 1.

Results and Discussion

The analysis shown in Table 1 were performed by the respective laboratories; the results shown in Table 3 were calculated from the analytical data.

Table 3. Emission Rates and Characterization of Emissions

Fine Particle Emission Rate (mg/kg fuel burned)	1.23 (Day 1) 3.54 (Day 2)	
Speciated Carbonyl Compounds Emission Rate (mg/kg fuel burned)	2.52 (Day 1) 0.79 (Day 2)	
Total Carbonyl Compounds Emission Rate (mg/kg fuel burned)	2.74 (Day 1) 0.96 (Day 2)	
Speciated NMOC Emission Rate (mg/kg fuel burned)	4.83 (Day 1) 0.98 (Day 2)	
Total NMOC Emission Rate (mg/kg fuel burned)	7.50 (Day 1) 1.85 (Day 2)	
Elemental and Organic Carbon (wt % of measured fine PM mass)	Without denuder[3]	With denuder[4]
Elemental Carbon	3.0 ± 0.4	13.8 ±3.1
Organic Carbon	84.6 ± 11.0	32.6 ± 8.0
Ionic Species[5] (wt % of measured fine PM mass)		
Chloride	NQ[1]	
Nitrate	NQ	
Sulfate	7.8 ± 0.6	
Potassium	6.6 ± 0.5	
Magnesium	ND[2]	
Calcium	ND	
Elemental Composition[6] (wt. % of measured fine PM mass)		
Sodium	0.18 ± 0.04	
Magnesium	0.17 ± 0.01	
Silicon	16.2 ± 2.5	
Phosphorus	0.09 ± 0.03	
Sulfur	3.7 ± 0.4	
Chlorine	0.64 ± 0.04	
Potassium	10.6 ± 0.6	
Calcium	0.76 ± 0.06	

[1]NQ - below quantitation limits
[2]ND- below detection limits
[3]Average of two filters, one from each day of testing
[4]Average of two filters, one from each day of testing
[5]Average of two filters from each day of testing with the exception of sulfate, which was below quantitation limits on the second day
[6]Average of two filters from the first day of testing. Error shown is the standard deviation of the results from the individual filters.

Discussion

Observed analytical results from the two days showed parallel results for volatile organic compounds, carbonyl compounds and PM-2.5 mass: Day #2 levels were approximately half the levels observed on Day #1. There were no significant observed differences in boiler or electrostatic precipitator operating parameters between the two days. Because only two test runs were performed, there is no way to resolve the apparent discrepancy. An explanation for the observed significant decrease in emission rates of both gaseous and PM-2.5 emissions

between the two test days could not be deduced with confidence.

Both gas phase and particle phase emissions from the wood-fired boiler were measured. Values reported are for the composition of gas and particulate matter emissions following cooling and dilution of the boiler stack gas rather than the in-stack exhaust gas composition and may therefore be considered representative of the emissions in the exhaust plume near the stack. Diluted source emissions reported in this way are more appropriate than in-stack for source-receptor models used for apportioning pollutants in the ambient air to the sources of the pollutants.

Elemental and organic carbon content of the PM-2.5 collected on quartz filters was found to be highly dependent on whether an XAD-coated denuder was inserted in the sampling line prior to the filter. The purpose of the denuder was to remove gas-phase semi-volatile organic compounds which otherwise might be adsorbed to the quartz filter, thereby resulting in a positive artifact. Without the denuder, the amount of organic carbon found on the quartz filter was 2.6 times the amount found with the denuder, thus providing confirmatory evidence for a positive adsorption artifact.

The ion mobility spectrometer system was operated on both test days, collecting data on particle size distribution in the range below 2.5 microns (the actual range monitored was 9 nanometers to approximately 400 nanometers). Analytical data are presented graphically as a plot of midpoint diameter of the particles vs. counts (an indirect version of number of particles in each size range). The size distribution profile for August 8 is shown in Figure 2; the profile for August 9 is similar. These data show that the distribution of particles is approximately bell-shaped in the size range monitored, with the largest number of particles at a midpoint diameter of approximately 140 nanometers on August 8 and 180 nanometers on August 9. The results for particles in this size range reflect the general difference in concentration for carbonyls, SNMOC and PM-2.5 mass between Day 1 and Day 2: a maximum of ~$6x10^4$ particles/cm^3 for Day 1 versus ~$0.8x10^4$ particles/cm^3 for Day 2. Thus, between the two test days, there appears to be a slight shift in the particle size distribution toward larger-diameter particles between Day 1 and Day 2, and a drop of a factor of about 7 in the concentration of particles observed between the two days.

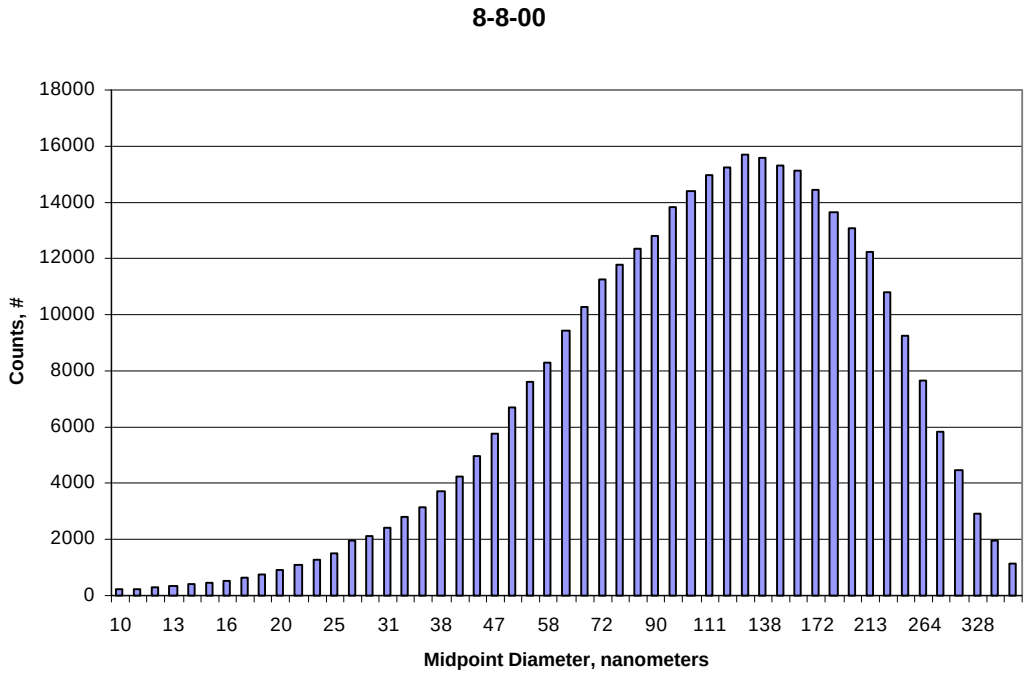

Figure 2

Individual organic compounds comprising the organic carbon fraction of the PM-2.5 emissions consisted mostly of polynuclear aromatic hydrocarbons, alkanes ($>C_{15}$), alkanoic acids ($>C_8$), and the iso- and anteiso-alkanes. Levoglucosan, a marker compound for biomass combustion, was found in the particulate matter but not in the relatively large amounts characteristic of open burning of biomass of woodstove combustion emissions. Resin acids (e.g., pimaric, isopimaric, and sandarapimaric acids) used as markers for softwood combustion and methoxyphenols used as markers for hardwood combustion were not found. Therefore, the organic compound emission profile for the wood-fired industrial boiler is very unlike profiles for residential wood-fired appliances (woodstoves and wood-burning fireplaces) and biomass open burning. This observation is not unexpected since the combustion regimes are very different for the two types of sources and since the boiler particulate matter emissions in this case were controlled by a multi-stage electrostatic precipitator whereas residential wood-fired appliance emissions are typically uncontrolled. Residential wood-fired appliances operate at much lower temperatures compared to industrial boilers, and the combustion process for woodstoves and fireplaces entails repeated cycling from an initial kindling phase through a final smoldering phase over the course of normal operation. Operation of an industrial boiler such as the one studied here involves charging the fuel at a fairly constant rate, and the combustion can be thought of as occurring in two stages: an initial stage in which the wood is gasified under pyrolysis conditions and a second stage in which the pyrolysis gases are essentially completely combusted in the presence of excess air. For all of these reasons, it is expected that the mass emission rates of both gaseous organic compounds and particulate matter from a well-controlled industrial wood-fired boiler would be much less than for a residential wood-fired appliance and that the organic compositional profiles would also be substantially different.

Acknowledgments
The efforts of the following people are gratefully acknowledged: from ERG, Dave-Paul Dayton, Mark Owens, Rob Martz, Amy Frame, Donna Tedder, Randy Bower, Joan Bursey, Ray Merrill, Carol Hobson; from EPA, Michael Hays and Kara Linna; from Arcadis, Geraghty & Miller, Inc., Yuanji Dong, Howard White, David Proffitt, and Tomasz Balicki. N. Dean Smith (EPA) was the Project Officer responsible for overall project performance.

Reference
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GENERATION OF EVALUATION STANDARDS FOR PERFORMANCE OF MONITORING METHODS AT LOW CONCENTRATIONS

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Monitoring methods promulgated by the U. S. EPA and the emerging measurement technologies that need laboratory analyses for characterization and quantitation are limited to checking only a few selected parameters that affect the measurements due to the difficulty in generating and the nonavailability of performance standards for laboratory analyses of the pollutants. Quality assurance and quality control of the stack gas testing and sampling system consists of testing flow rates, flow measurement accuracy, leak tests, flow rate control, ambient temperature measurement accuracy, pressure measurement accuracy, filter temperature control during sampling, correct determination of elapsed time and average volumetric flow rate determination.

There is a lack of availability of performance samples for evaluating the analytical performance of metals analysis laboratories for EPA Method 29 or Method 5. At best, presently, performance standards are prepared by evaporating National Institute of Standards and Technology (NIST) standard metal salt solutions of inappropriate concentrations on a filter paper and sending the "unknown" sample to participating laboratories for performance evaluation. This practice totally disregards the distribution of the sample on the filter, interaction of analytes with filter materials and the processes used for the extraction of analytes.

We have developed a system to generate aerosols of known metallic compounds such as oxides and nitrates and of known particle size distributions for the preparation of x-ray standards. The system can be readily modified to make an excellent performance evaluation (PE) system for stationary source monitors. The particle size can be varied from 0.1 to several micrometers by proper selection of operating conditions. The data developed for analytes such as zinc, sulfur, nickel, chloride and bromine for use as standards in x-ray fluorescence (XRF) analyses were cross-checked against analyses of filters by atomic absorption (AA) spectroscopy. It was found that, after solving certain operational problems, the aerosol output was reproducible, is stable over several hours and provides a superior means for developing PE standards.

The particle generating system has promise to prepare custom-made combinations of analytes over a wide distribution of sizes by varying the operating conditions to simulate emissions at low concentrations. The data for some analytes over a low concentration range needed by the XRF spectrometer indicate that the spectrometer response, in a given range, is proportional to the concentration on the filters giving a linear correlation. The preparation of a set of calibration standards for several analytes will be followed by experiments to prepare

standards to simulate flue-gas particles by collecting the metal analytes embedded in low-metal-containing carbon.

LABORATORY CONTROL SAMPLE (LCS) STUDY UPDATE

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ABSTRACT / INTRODUCTION / SUMMARY

The Department of Defense (DoD) Environmental Data Quality Workgroup (EDQW) Quality Assurance Task Action Team (QA-TAT) in its work to develop the DoD Quality Systems Manual (QSM) for Environmental Laboratories has conducted a study to establish laboratory control sample (LCS) control limits (CLs) for environmental laboratories that conduct chemical testing for DoD. The LCS-CLs are based on actual LCS data from several laboratories currently working for DoD. Data was gathered for all target analytes, pooled and statistical analyses performed, including outlier tests and analysis of variance (ANOVA) of key method variables.

The pilot study for this effort was conducted last year for SW-846 Method 8270C, and those results were presented at the 2000 WTQA Conference. The LCS Study Update will present the LCS control limits generated for the remaining chemical parameters within aqueous and solid matrices, including VOCs by 8260B, Pesticides by 8081A, PCBs by 8082, Herbicides by 8151A, PAHs by 8310, Explosives by 8330, various metals by ICP (6010B) and mercury by 7470A and 7471A.

Other DoD policy issues to be reflected within the DoD QSM, and general observations from the study will be presented, including target analytes found to be poor performing compounds and how to deal with them, the concept and use of sporadic marginal exceedances when evaluating LCS and sample batch acceptance, and necessary corrective actions based on LCS failures. ANOVA results will also be presented.

It is not the intent of the EDQW QA-TAT to downplay the importance of developing project-specific data quality objectives (DQOs). Laboratories conducting analysis for DoD must use the project-specific control limits or other measurement quality objectives based on project DQOs. In addition, any project-specific contaminants of concern are not subject to variances, such as sporadic marginal exceedances, therefore the importance of communicating this project-specific information in the form of DQOs to the laboratory becomes critical to both parties. However, when no project contaminants of concern or measurement quality objectives are identified, or when a general analytical suite of chemical parameters are employed with no other information, the DoD LCS-CLs are to be used as the default. LCS-CLs are being established to maintain a level of consistency in the expected quality for analytical data generated for DoD programs, while acknowledging the ‘experimental’ nature of the business.

DoD personnel and other stakeholders can also benefit from the study results. The EDQW QA-TAT hope that DoD personnel will use the LCS-CLs during the planning process to evaluate whether current SW-846 protocols meet the quality expectations for their project’s contaminants of concern. When the control limits show that general method performance is

not satisfactory, a dialogue with experienced laboratory personnel is needed to identify where PBMS or method modifications should be used to better support the intended use of that data. Concise and open communication between DoD project personnel and the laboratory covering pertinent issues of project DQOs, specific data needs and measurement quality objectives are essential. Another benefit the LCS-CLs provide is that they may be used as a benchmark to evaluate a laboratory's or new technology's performance. Through the comparison of the LCS-CLs to in-house statistical limits, one may evaluate their performance against a more robust data set. The results are compelling, and allow those not working at the lab bench to gain insight on what is routinely achievable by the environmental industry today.

DOD LABORATORY QUALITY SYSTEMS MANUAL (QSM) UPDATE

B. Batschelet

No abstract available.

EPA/DOD STANDARDIZATION EFFORTS (QA MATRIX)

R. Runyon

No abstract available.

ENVIRONMENTAL ANALYSES OF AGENT DEGRADATION PRODUCTS

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ABSTRACT

In support of projects for the U.S. Army Environmental Center in the late eighties and early nineties, DataChem Laboratories, Inc. developed methods for the analysis of agent degradation products on military sites. This paper will present developed methods for the agent degradation products listed below:

Analysis Technique	Agent Degradation Products
Gas Chromatography with Flame Photometric Detection	Dimethyldisulfide 1,4-Oxathiane 1,4-Dithiane
Gas Chromatography with Flame Photometric Detection	Diisopropylmethylphosphonate (DIMP) Dimethylmethylphosphonate (DMMP)
Gas Chromatography with Sulfur Chemiluminescence Detection	Thiodiglycol
Ion Chromatography with Conductivity Detection	Fluoroacetic Acid Chloroacetic Acid Methylphosphonic Acid (MPA) Isopropylmethylphosphonic Acid (IMPA)

INTRODUCTION

An environmental pathway for each degradation product is presented along with a description of the analytical technique used for the analysis of environmental samples. Performance data for each method is tabulated to validate the use of these methods and finally the description of several DoD projects is presented.

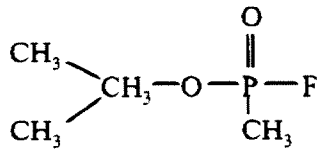
AGENT DEGRADATION PRODUCTS[1,2]

Chemical warfare agents (CWAs), when released to the environment, “weather” and break down in soil and water. Therefore, contamination assessment at sites with past CWA releases must rely upon determining the presence and amount of breakdown products as well as the

presence and amount of any CWAs that may still remain. In this section the environmental fate and breakdown products of three common CWAs (GB, VX and HD) are discussed and summarized.

The most thoroughly studied CWA breakdown process is base-catalyzed hydrolysis because many of the defensive chemical decontamination procedures employ it. CWAs are hydrolyzed similarly by water in the environment. However, the precise effects of clays, humic acids, photodecomposition, and microbial action in the environmental fate of CWAs are not well understood.

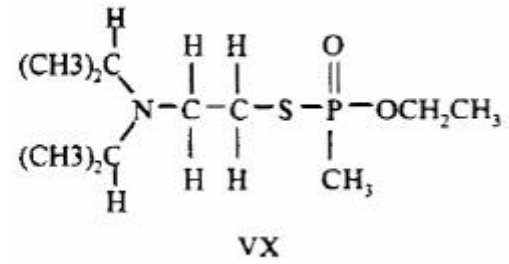
GB



GB

GB (CAS No. 107-44-8, Sarin, or O-isopropylmethylphosphonofluoridate) is infinitely soluble in water and will hydrolyze under acidic, neutral and basic conditions. The rate of hydrolysis is slowest in the pH range 4 to 6. GB has a hydrolytic half-life of about 160 hours at pH 5 and 25 degrees Celsius (°C). The rate of hydrolysis becomes more rapid below pH 4 and above pH 6, increasing rapidly with increasing hydroxide ion concentration. At 25 °C and at pH 10 the half-life of GB is 5 minutes. The alkaline hydrolysis products of GB are fluoride ion and isopropyl methylphosphonic acid (IMPA). Some starting materials, methylphosphonic difluoride and diisopropylmethylphosphonate (DIMP), also may be present in GB as impurities. Methylphosphonic difluoride hydrolyzes to form methylphosphonic acid (MPA) and fluoride ion. At sufficiently high pH, DIMP undergoes slow hydrolysis to form IMPA, which then hydrolyzes further to form methylphosphonic acid (MPA). Typical environmental markers for GB contamination are IMPA, MPA and DIMP. Dimethylmethylphosphonic acid (DMMP) is a precursor in some methods of manufacture of GB and can be associated with GB contamination at production facilities. It is also used as a CWA simulant. Knowledge of site history is necessary to evaluate the significance of DMMP at a site.

VX

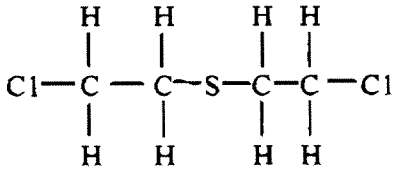


VX

VX (CAS No. 50782-69-9, O-ethyl S-[(diisopropylamino)ethyl] methylphosphonothioate) is not subject to acid catalyzed hydrolysis but does undergo water-mediated and hydroxyl ion-catalyzed hydrolysis. The hydrolysis of VX proceeds by multiple pathways and results in a more complex set of products than the hydrolysis of GB. VX hydrolysis rates are slower than

those of GB. For example, at pH 10 and 25°C the half-life of VX in water is 40.5 hours compared to 5 minutes for GB. At pH 5 and 25°C the half-life of VX in water is 2,342 hours compared to 160 hours for GB. Across the entire pH range the P–S bond is cleaved to give two primary products: ethylmethylphosphonic acid (EMPA) and 2-diisopropylaminoethanethiol (DESH). EMPA further decomposes to MPA. Bis(2-diisopropylaminoethyl) disulfide [$(DES)_2$] is formed by air oxidation of DESH. In the middle and higher pH ranges additional reaction pathways contribute to the mix of hydrolysis products. In addition to P–S bond cleavage, the P–O–C bond to the ethoxy group and the C–S bond are also broken. The product of ethoxy group cleavage, EA 2192, is comparatively stable towards hydrolysis. Finally, C–S bond cleavage in the neutral pH range results in the formation of O-ethyl methylphosphonothioic acid, diisopropylaminoethyl sulfide and possibly other minor products. Typical environmental markers for VX contamination are EMPA, MPA and $(DES)_2$.

HD



H/HD

HD (CAS No. 505-60-2) is also called distilled Levinstein Mustard, or distilled Sulfur Mustard. Mustard degrades in the environment by a stepwise hydrolysis with positively charged ion intermediates. The nature of the hydrolysis products of HD is highly dependent upon environmental conditions. Under ideal conditions (a large excess of water, high pH and adequate stirring) HD can be hydrolyzed almost exclusively to thiodiglycol and chloride ion. As the HD to water ratio decreases, 1,4-oxathiane, 1,4-dithiane, 2-vinylthioethanol and mustard chlorohydrin are formed in addition to polysulfides and some uncharacterized compounds. Some of the compounds identified as breakdown products of mustard in the environment may be impurities from the manufacturing process that were not removed by distillation. Bulk HD can persist deep in the soil or under quiescent water for years. This persistence is thought to be the result of a layer of oligomeric polysulfide degradation products formed by limited hydrolysis. Typical environmental markers for well-dispersed HD contamination are thiodiglycol and 1,4-oxathiane. Knowledge of the site may indicate whether analyzing for one or more of the sulfides or disulfides is necessary.

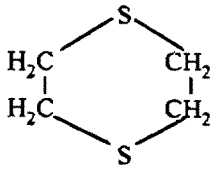
Table 1. Properties of GB, VX and HD

Property	GB	VX	HD
Formula	$C_4H_{10}FO_2P$	$C_{11}H_{26}NO_2PS$	$C_4H_8Cl_2S$
Molecular Weight	140.1 g/mol	267.38 g/mol	159.08 g/mol
Vapor Pressure (torr)	2.94/25°C	6.2×10^{-4}/25°C	0.1059/25°C
Log K_{OW} (est.)	0.15	2.10	1.70
Aqueous Solubility (g/L)	Miscible in all proportions.	30 g/L at 25°C	0.92 g/L at 22°C

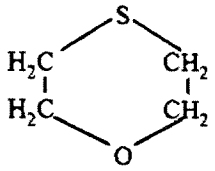
Environmental Markers	IMPA and MPA DIMP (an impurity) and DMMP (if a manufacturing site)	EMPA and MPA $(DES)_2$	Thiodiglycol and 1,4-oxathiane Various sulfides and disulfides. Dimethyl disulfide (DMDS) and dithiane are examples.

ANALYSIS METHODS

Determination of Organosulfur Compounds by Gas Chromatography



1,4 - Dithiane



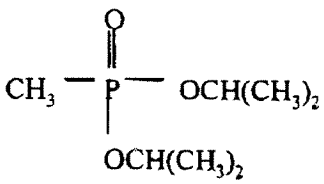
1,4 - Oxathiane

Three breakdown products of HD or sulfur mustard (dimethyldisulfide, 1,4-oxathiane and 1,4-dithiane) can be quantitatively determined in the same gas chromatographic analysis. This method provides reporting limits as low as 2 µg/L for water samples. Since all three compounds contain sulfur, a flame photometric detector (FPD) in the sulfur mode is used. The FPD detector is specific for the detection of compounds containing sulfur; this eliminates many possible coeluting interferences, and increases the qualitative information provided by the analysis.

An aliquot of the sample extract is injected into a Perkin Elmer Autosystem gas chromatograph with FPD. Any equivalent gas chromatographic system will provide acceptable results, however, older FPD detectors without electronic linearization are extremely difficult to use because actual detector response over the calibration range cannot be approximated with a single calibration curve. Even with electronic linearization, the response is not totally linear and the best fit for initial calibration data is achieved using a quadratic equation.

Separation is accomplished using a 30-meter narrow-bore (0.25µm) DB-1 capillary column with 0.25-µm film thickness. A second column analysis is not performed because the specificity of the detector, along with the retention time, provides sufficient qualitative information.

Determination of Diisopropylmethylphosphonate and Dimethylmethylphosphonate

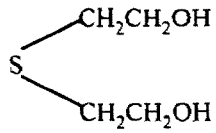


DIMP

Diisopropylmethylphosphonate (DIMP), an impurity in GB production which is used as a marker for GB, and dimethylmethylphosphonate (DMMP), a GB precursor, are quantitatively analyzed using a gas chromatograph equipped with a flame photometric detector (FPD) in the phosphorous mode. The FPD detector is specific for compounds containing phosphorus and interferences are eliminated.

Separation is accomplished using a 30-meter wide-bore (0.53µm) DB-1 capillary column with 1.5-µm film thickness. This method provides reporting limits below 1 ppb in water for DMMP and DIMP.

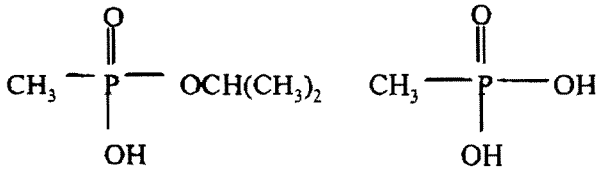
Determination of Thiodiglycol



Thiodiglycol

Thiodiglycol, a breakdown product of HD, is also an organo-sulfur compound and presents some unique challenges because of its high solubility in water. Traditional approaches using solvent extraction were not successful because the extraction recovery was low and not reproducible. The development of a highly sensitive sulfur chemiluminescence detector (SCD) has made it possible to inject a water sample directly without concentration and still achieve a detection level of 10 to 20 ppb. A Hewlett Packard 5880 GC interfaced with a Sievers 355 Sulfur Chemiluminescence Detector is used for analysis. Separation is accomplished using a 30-meter X 0.53-µm J&W Scientific DB Wax column with 1.0-µm film thickness.

Determination of Organic Acids by Ion Chromatography



IMPA MPA

Ion chromatography can be used to determine all of the following agent decomposition products: methylphosphonic acid (MPA), the final breakdown product of GB and VX; Isopropylmethylphosphonic acid (IMPA) another breakdown product of GB; fluoroacetic acid and chloroacetic acid which are thought to be breakdown products of GB and HD respectively. A Dionex Model 300DX ion chromatograph with conductivity detector is used. Reporting limits are in the 200 ppb range for water samples.

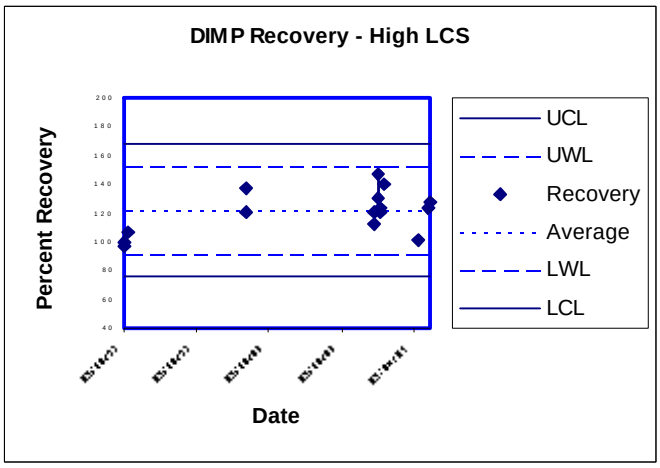
METHOD PERFORMANCE DATA

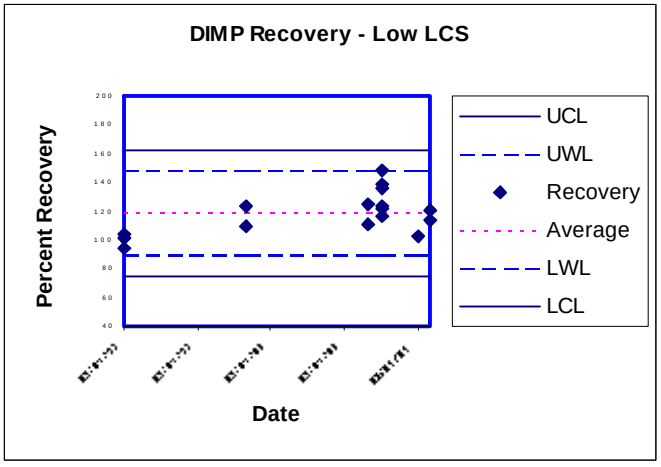
Table 2 summarizes method performance criteria and quality control procedures for each method

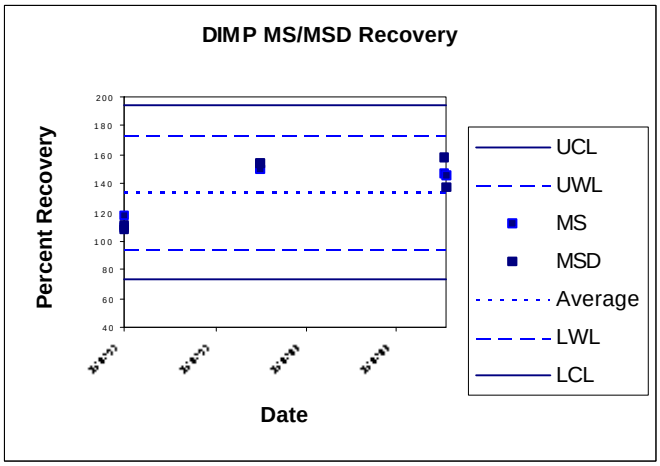
Table 2. Method Performance Criteria

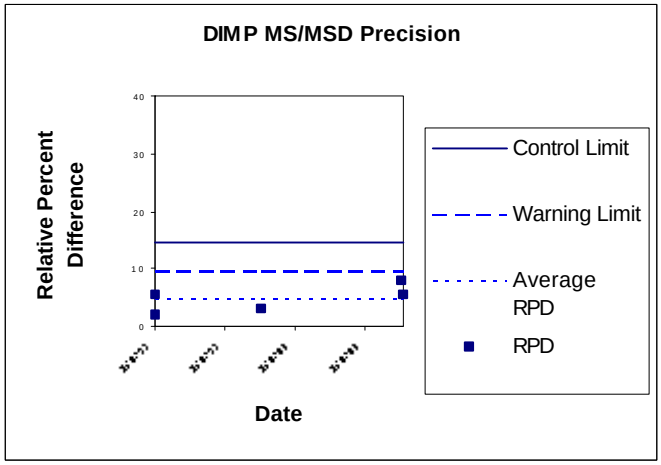
Method	DIMP/DMMP	Thiodiglycol	IMPA/MPA	Organosulfurs 1,4-Dithiane 1,4-Oxathiane
Calibration Levels	6.00	6.00	6.00	7.00
Calibration Type	Quadratic Fit	Quadratic Fit	Quadratic Fit	Linear Fit
Calibration Criteria Corr. Coef.	0.995	0.995	0.995	0.995
ICV Source	Same Source Different Person	Different Source	Same Source Different Person	Same Source Different Person
CCV Frequency	Every 10 samples	Every 10 Samples	Every 10 Samples	Every 10 samples
ICV/CCV Criteria	25% from True Value	25% from True Value	15% from True Value	25% from True Value
Method Blank	One per Batch	One per Batch	One per Batch	One per Batch
Low LCS	One per Batch	One per Batch	One LCS per Batch	One per Batch
High LCS	Two per Batch	Two per Batch		Two per Batch
MS/MD or MSD	Not Required	MS/MSD per Ten Sample Batch or Client Specs	MS/MD or MSD per Batch	MS/MSD per Ten Sample Batch or Client Specs

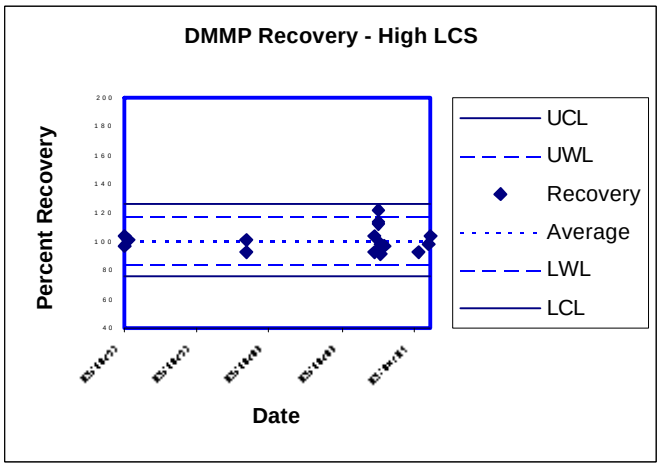
Accuracy and Precision Charts for DIMP and DMMP.

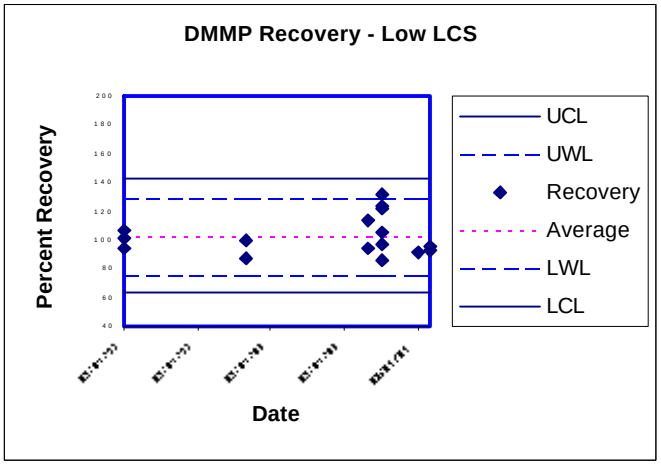


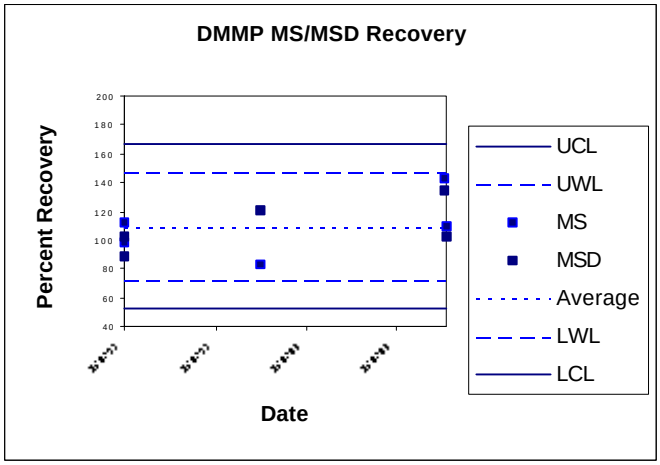


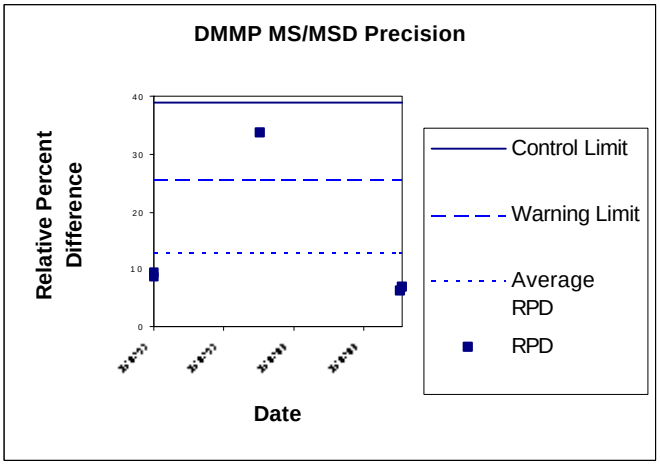












QC Charts for thiodiglycol, 1,4-dithiane, 1,4-oxathiane, IMPA and MPA are similar to those presented above and will be shown during the oral presentation at WTQA2001.

DoD PROJECT SUMMARIES

Rocky Mountain Arsenal (Colorado)

Rocky Mountain Arsenal (RMA) occupies approximately 27 square miles of prairie in southern Adams County, Colorado. It is located 10 miles north of the Denver metropolitan area and east of Commerce City, Colorado. RMA was established in 1942 as a chemical weapons manufacturing site. Most of the Arsenal was placed on the National Priorities List (NPL) in 1987 with the Basin F Area added in 1989.[3]

Basin F contained runoff from: Sand Creek Lateral, a drainage ditch which ran from South Plants; spillage or leakage from broken pipes or faulty joints, and manholes in the sewer lines; some spillage or leakage from operation of the Deep Injection Well; and soil contaminated by windblown dust.[3]

IMP is not known to occur naturally in the environment. Approximately 130,000 pounds of DIMP were generated at RMA and discharged into unlined basins. This resulted in the contamination of groundwater both on and off the Rocky Mountain Arsenal.[3]

DataChem Laboratories, Inc. (DCL) developed and validated methods listed in this paper in conjunction with work being completed at RMA. These methods were used to analyze remedial investigation samples from Basin F and Site A, as well as groundwater monitoring throughout the site.

Deseret Chemical Depot (Utah)

The primary mission of the Deseret Chemical Depot (DCD) is storage of a large percentage of the United States stockpile of chemical munitions. The depot also supports weapons demilitarization including research and development activities. The DCD is located approximately 12 miles south of Tooele, Utah, in Tooele county.[4]

DCL has completed soil and groundwater investigations using methods for thiodiglycol and organosulfur compounds to support the ongoing efforts at DCD.

Aberdeen Proving Ground (Maryland)

Aberdeen Proving Ground (APG), the Army's oldest active proving ground, was established on October 20, 1917, six months after the United States entered World War I, to provide the military a facility where design and testing of ordnance material could be carried out in close proximity to the nation's industrial and shipping centers. The post officially opened on December 14, 1917, and the first gun was fired on January 2, 1918.

APG's Edgewood Area has been a center for chemical warfare research and development since it was established. From the trenches of France and Belgium in World War I to the desert battlefields of Iraq nearly 75 years later, the work done at APG has contributed to the defense and safety of American forces threatened by chemical weapons.[5]

DCL continues to be involved ongoing, providing analysis of soil, groundwater and vegetation for all agent degradation products.

Dugway Proving Ground (Utah)
The mission of Dugway Proving Ground (DPG) is to test U.S. and Allied biological and chemical defense systems, perform Nuclear Biological Chemical survivability testing of defense material, provide support to chemical and biological weapons conventions, and operate and maintain an installation to support the test mission. DPG, covering 798,855 acres, is located in the Great Salt Lake Desert, approximately 85 miles southwest of Salt Lake City, Utah, in Tooele County. Surrounded on three sides by mountain ranges, the proving ground's terrain varies from level salt flats to scattered sand dunes and rugged mountains.[6]

DCL provides support to DPG for alternative destruction technology by confirmation analysis for agent degradation products.

SUMMARY

Chemical Warfare Agents (GB, VX and HD) when released to the environment weather and break down producing degradation products like DIMP, DMMP, 1,4-Dithiane, 1,4-Oxathiane, Thiodiglycol, IMPA and MPA. Some of these compounds are actually precursors to the production of CWAs. Methods for the analysis of agent degradation products were developed and validated in conjunction with the U.S. Army Environmental Center and have performed well over the past decade on a variety of environmental soil and water matrices. Data is presented to support ongoing method performance. Calibration control, method quality control and chromatographic performance meet or exceed standard analytical practices in the environmental marketplace. These methods have performed well on projects producing valuable data to support investigation and monitoring activities.

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1. The Detoxification and Natural Degradation of Chemical Warfare Agents, Ralf Trapp, Taylor & Francis: London, 1985. [SIPRI Chemical & Biological Warfare Studies, No. 3]
2. Agent / Decontamination Chemistry Technical Report, US Army Test and Evaluation Command (TECOM) Technical Support, Phase I, Prepared for Environmental Quality Office, US Army Test and Evaluation Command, David H. Rosenblatt, Mitchell J. Small, Todd A. Kimmel, Andrew W. Anderson, Argonne National Laboratory, October 19, 1995. [Note: This U.S. Army technical report was prepared for regulatory and public review and has been released for that purpose.]
3. http://www.pmrma-www.army.mil/htdocs/rma.html
4. http://www.eq.state.ut.us/eqshw/cds/DCDHP1.htm
5. http://www.apg.army.mil/
6. http://www.fas.org/nuke/guide/usa/facility/dugway.htm

LABORATORY HEALTH AND SAFETY WITH DOD SAMPLES

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ABSTRACT

Severn Trent Services (STL) has handled many Department of Defense related projects. Samples from DoD sites may contain additional hazards beyond the *normal* carcinogens, mutagens, toxics, corrosives, caustics, oxidizers and flammables that environmental labs commonly handle. DoD samples may contain chemical warfare agents and degradates which are more toxic than common environmental pollutants. Also, DoD samples may contain high levels of incendiary chemicals thus presenting an explosion hazard. Lastly, some DoD samples may have radioactive contamination that necessitates different processes and procedures.

Special health and safety precautions and procedures may include any of the following: general DoD awareness training, specific training related individual chemical agents including symptoms and first aid, prescreening of samples in the field or at a specially equipped laboratory and notification of area health and safety organizations including material safety data sheets.

INTRODUCTION

Environmental laboratories handle samples daily that have many health and safety risks associated with them. These *normal* samples may contain components that are irritants, flammables, carcinogens, mutagens, endocrine disrupters, toxics, corrosive acids or bases, oxidizers and occasionally lachrymators. Environmental analysis on samples collected from DoD sites may present additional risks beyond the usual ones that environmental labs have become proficient at handling. There are three main hazard areas: increased toxicity, explosive potential and radioactivity. Chemical agents were specifically made to negatively affect human health when exposed. Some of the agent precursors and degradation products also have significant health effects. Explosive constituents are common at DoD sites because of use either as propellants or explosive charges. Radioactive isotopes may also be present from either nuclear weapons or nuclear power sources. Although the specific details are different between the three hazard types, the general concerns and processes are similar. The overall process by which these DoD specific health and safety issues are added to a conventional environmental health and safety program will be illustrated using the chemical agent example. Then, differences related to explosive and radioactivity hazards will be noted.

CHEMICAL AGENTS

As with all environmental testing projects the analyte list must be established up front. Depending on the project the chemical agents, precursors and degradates may be analytes of interest. If these compounds were not actual analytes, then these chemicals would be considered other hazardous constituents. Knowing the sample matrix types is important since

this may affect the severity of some hazards. Specialized training is needed to address the new hazards. Often there are several agencies or facilities in the community that should be notified so they can be appropriately prepared should an emergency response be necessary. Screening of the samples prior to arrival at the environmental lab is important to make sure the likely hazard is within the limitations of the health and safety program. Lastly, special sample handling and disposal procedures may be needed.

Most environmental testing of DoD samples involve conventional environmental analytes such as metals, volatile organic compounds and semi-volatile organic compounds. Most STL projects have not included testing for the chemical agent, precursors or degradates. Chemical agents such as agent HD (mustard gas), precursors sulfur dichloride, hydrogen chloride and ethylene oxide and degradates diethylene disulfide, 1,4-oxathiane and thiodiglycol are usually viewed as other hazardous sample constituents.

Sample matrix types may include the usual air, water, soil and sediment. In addition, organic and inorganic wastes may present special challenges for both safe handling and analysis. Unusual sample types necessitate careful case by case considerations and detailed communication between client and lab.

Employee training, either by inside or outside experts, is needed to cover new information that is not normally necessary for traditional environmental analyses. Subject areas include: historical background, agent descriptions, hazards of analytes or other potential sample components, signs and symptoms of exposure and exposure responses. Typically a test or quiz is used to demonstrate and document that the employee has the necessary knowledge. Several health and safety organizations should be notified of the change in potential lab hazards. This notification may include sending material safety data sheets to the local emergency medical system, fire department, HAZMAT team and hospital.

Sample prescreening prior to receipt at the environmental laboratory is essential to protect the health of employees at environmental labs that are not equipped to handle high concentrations of chemical agents. Screening may be done in the field or at a specially equipped lab. Screening results documenting acceptable hazard levels must accompany or precede the samples.

Sample handling and disposal procedures should be established for several scenarios: receipt of agent contaminated sample, broken sample container and disposal of unused sample. During the preliminary setup discussions it should also be determined if any facility modifications are needed. If they are necessary, implement a plan to ensure the changes are complete in advance of sample receipt.

EXPLOSIVES AND PROPELLANTS

The general concerns and questions are similar to those described above with regard to chemical agents. Specific details will vary in some areas. Typically the explosives and degradates are target analytes for the overall project though for other conventional tests the explosive compounds would be considered as “other hazardous constituents”. Training details will differ, particularly in the sample preparation area. Sample screening is accomplished by different chemical and instrumental processes, but the need is just as great. Handling and

disposal processes must also take into account the explosion hazard.

The overriding principle for sample preparation and analysis is: Do not heat the sample or its extract. Neat explosive materials must by vacuum dried without heating. Before preparation all solid samples should be inspected for lumps or grayish-white powder to confirm that field screening has not missed a high level sample that may present an explosion hazard. Sample preparation for explosive analysis generally does not include a solvent concentration step because this step commonly requires the concentrated extract to be heated.

RADIOACTIVITY

The general concerns and questions are similar to those described above with regard to chemical agents. Specific details will vary in some areas. Typically the *alpha*, *beta* or *gamma* emissions or radioactive isotopes themselves are the target analytes. If other conventional tests are needed an appropriately equipped mixed waste lab should be employed for radioactive samples. Training details will differ with regard to safe handling of potentially radioactive material. Sample screening is accomplished by different chemical and instrumental processes, but the need is just as great particularly if non-radioactive samples are to be selected and sent to a conventional environmental lab. Handling and disposal processes must also take into account the radioactivity hazard.

Specific training areas to be covered are: radioactivity and decay, characteristics of ionizing radiation, man made radiation sources, acute effects of exposure, associated risks, pre-natal considerations, dose equivalent limits, modes of exposure, basic protection measures, contamination control, personnel decontamination, emergency procedures and federal, state and STL protection policies.

SUMMARY

The health risks associated with conventional environmental testing are significant but are handled on a daily basis. Expanding the sample and analyte range to include Department of Defense related samples requires consideration of additional risks related to chemical agents, explosives and radioactivity. The laboratory must know its capabilities so that employees may safely live within the limitations.

ACKNOWLEDGEMENTS

Many STL employees have contributed to developing the knowledge base summarized here. In particular the authors are indebted to Bill Deckelman, Joel Kempema, Linda McWhirter, Louis Osborne and Nathan Nunn.

ON-SITE CHARACTERIZATION OF EXPLOSIVE RESIDUES IN SOILS AND ON RANGE SCRAP USING GC-TID ANALYSIS

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ABSTRACT

An economical on-site method has been developed for rapid identification and quantification of frequently detected nitroaromatic, nitramine and nitrate ester explosives (e.g., TNT, TNB, RDX, HMX, NG, 2,4-DNT, 2,6-DNT, PETN, 2Am-DNT, 4Am-DNT, Tetryl, 1,3-DNB) in soil and on range scrap. The method combines quick and simple sample preparation procedures, colorimetric wet chemical pre-screening and gas chromatographic (GC) analysis. The final analysis step uses a GC equipped with a thermionic ionization detector (TID) that is selective for compounds containing nitro (NO_2) functional groups. Quantitative results using the GC-TID method were in good agreement with results from HPLC (Method 8330) or GC electron capture (Method 8095) for the analysis of the same sample extract and for sample splits.

INTRODUCTION

The ability to quickly characterize the spatial distribution of contamination over a large area and to minimize the number of non-detect samples sent off-site for analysis are two common incentives for using on-site methods. On-site rapid colorimetric screening and subsequent analysis by gas chromatography–thermionic ionization detection (GC-TID) meets these objectives for the suite of explosives that often coexist in soils and on range scrap at military training facilities and other defense-related sites. Moreover, this assay fills an existing gap between the capabilities of the current EPA-approved on-site methods (4050, 4051, 8510 and 8515) and laboratory-based methods (8330 and 8095), is field rugged and requires minimal auxiliary support. This paper describes a procedure that uses a simple colorimetric analysis to estimate the proper dilution and GC-TID detection for contaminant identification and quantification. In addition, information will be provided on comparisons between GC-TID analysis and Methods 8330 and 8095.

MATERIALS AND METHODS

A qualitative and semi-quantitative visual colorimetric test to screen on-site for explosive residues can be performed using the Expray kit (Plexus Scientific, Silver Spring, MD). The Expray kit comes in a small, lightweight (less than 1.4 kg) case that contains several sheets of test paper and three aerosol cans for dispensing chemical reagents. The first aerosol can tests for the presence of polynitroaromatics, the second for nitramines and the third for inorganic nitrates.

The GC used was the Model 8610C (SRI Instruments, Torrance, CA) equipped with a heated (250°C) TID detector, a heated (225°C) on-column injection port and an internal air

compressor. This instrument currently sells for less than $9K and requires a personal computer ($1K) for controlling oven temperature programs and for collecting and handling data. Separations were performed on either a metal or glass Crossbond 100% dimethyl polysiloxane column (DB-1), 15 m × 0.53-mm i.d., 0.5 µm film thickness. Injections of 1 µL were made manually with a 10-µL glass syringe (SGE). The carrier gas was high-purity nitrogen flowing at 37 mL/min, and the TID potential was set at –3.40 V. In addition, air was supplied to the detector from the onboard compressor at a rate of approximately 15 mL/min. Using an oven temperature program of 95°C ramped at 10°C/min to 105°C, then ramped from 105° to 240°C at 40°C/min, there was baseline resolution between many of the explosive analytes listed in Method 8330. Sample injections can be made about every 7.0 min (Hewitt *et al*., 2001).

Calibration Standards

Analytical standards of the 14 explosives-related analytes listed in Method 8330, as well as nitroglycerine and PETN, were purchased either as a mixed stock standard (each analyte at 1.00 mg/mL) or individually from AccuStandard, Inc. (New Haven, CT). These stock standards were specially prepared using acetone as the solvent. The preparation and handling of mixed-analyte working standards was reported elsewhere (Hewitt and Jenkins, 1999).

Sample Preparation

To screen surfaces of range scrap, either the entire piece was submersed in acetone or the exposed surface was wiped (rubbed) with an acetone-moistened cotton swab held with metal tweezers (Hewitt, 2001). To estimate the surface concentration, the surface area of the piece submersed or swabbed should be measured. Moreover, the swab should be air-dried prior to extraction with 5 mL (or more) of acetone. For qualitative information, an area estimate is not necessary, and if a cotton swab is used, it can be placed directly into the barrel of a 5-mL disposable plastic syringe, followed by 1 mL of acetone.

Soil samples were prepared by extracting 1.0 to 40 g of field-moist soil with a one-to-five-fold greater volume of acetone (i.e., 1:1 to 1:5). Extractions were performed in either glass or plastic bottles by manually shaking the soil / solvent slurry several times for 30 seconds over a 30-minute period.

Following extraction, an aliquot of the acetone was passed through a 25-mm Millex FH (0.45-µm) filter that was attached, via a Luer-Lok™ fitting, to a disposable 3-mL plastic syringe. The filtered extract was directly transferred to a 2-mL amber deactivated glass vial.

Colorimetric screening was performed by transferring a 5-mL aliquot of solvent extract to a test sheet. Several (6 to 12) sample extracts can be screened simultaneously by pre-marking the test paper and carefully placing each aliquot. After allowing the acetone to evaporate, the surface of the test sheet was sprayed per kit instructions. If color appears following application of the first aerosol, then polynitroaromatics (e.g. TNT, TNB, DNT, picric acid, tetryl, etc.) were likely present. Some of the colors that may appear upon the application of this first aerosol are blue, red or orange. A bluish color appears when 2,4-DNT or 2,6-DNT is the dominant compound, a reddish-brown color appears for TNT and TNB, and an orange color for tetryl and picric acid. After application of spray from the second aerosol can, the formation of a pink color indicated the presence of nitramines or nitrate esters (e.g., RDX, HMX, NG, PETN, NC,

NQ and/or tetryl). Application of the first two aerosol cans allowed for the sequential detection of both polynitroaromatic and nitramines. If there was no color development, then the sample was sprayed with the third aerosol can. The development of a pink color after applying the third aerosol indicated the presence of an inorganic nitrate (ammonium, potassium, sodium, barium, strontium nitrate or black powder).

Visual and Instrument Calibration

A visual scale for the colorimetric screening test was prepared by spraying (see above) 5-µL aliquots of 10-, 100-, and 1000-mg/L standards of TNT and RDX after they had been placed on test sheets. All six aliquots were placed on the same sheet; however, the TNT standards had to be covered when applying the second aerosol. This screening method can detect the presence of 0.05 µg of explosive analyte when concentrated in a discrete location on a white surface. In general, the color intensity changes from a very light shade for 0.05 µg to a distinct light color for 0.5 µg and to a dark color for 5 µg.

For GC-TID, a five-point calibration curve is recommended for each analyte of concern. This number of standards allows non-linear models to be used when necessary. A non-linear model (quadratic through the origin) should be chosen when the linear regression through the origin fails to establish a correlation coefficient (r) of greater than 0.990. Calibration checks should be made after every five samples by randomly running one of the four highest working standards. When the calibration model fails to establish a concentration within ±20% of the expected value for a standard, re-calibration should be performed. The concentrations of the working standards ranged anywhere from 0.01 to 50 µg/L, depending on the analysis objectives. Table 1 shows MDLs obtained for spiked Ottawa sand. Typical chromatograms are available elsewhere (Hewitt *et al*., 2001).

Table 1. Method detection limits (MDLs) based on matrix (Ottawa sand) spike samples.

Compound	MDL (mg/kg)
NG	0.10
1,3-DNB	0.012
2,6-DNT	0.0054
2,4-DNT	0.0016
TNB	0.0024
TNT	0.0016
RDX	0.0094
4AmDNT	0.010
2AmDNT	0.0068
Tetryl	0.0017
HMX	0.027

Column: DB-1, 15 m, 0.5-µm film.

EXPERIMENTS

Three experiments were conducted: a) a quantitative assessment of explosives residues on a fragment removed from a hand grenade that had not properly detonated (“low order”) and on quality assurance coupons (explosives-spiked metal plates [Hewitt, 2001]), b) a qualitative assessment of explosives residues on the fins of two 120-mm mortar rounds after being fired,

and c) an analysis of several soil sample extracts and soil sample splits. The colorimetric screening step was only used with the soil samples since analyte concentrations were either known or were expected to be low on the other materials.

Two of four metal coupons (1.5- × 1.5-cm rusted steel plate) spiked with approximately 1 mg of TNT, RDX and HMX (Hewitt, 2001) and a 2.8-cm^2 fragment of a hand grenade casing were each wiped with an acetone-moistened cotton swab. The remaining two coupons, two wiped coupons, the hand grenade fragment and the three air-dried cotton swabs were then submersed in acetone. Table 2 compares the GC-TID and Method 8330 concentration estimates obtained for the acetone extracts of these samples.

Table 2. Comparison between GC-TID and Method 8330 for extracts of sample wipes and solvent immersion samples.

	Solvent extract (mg/L)					
	TNT		*RDX*		*HMX*	
	*TID**	*HPLC***	*TID*	*HPLC*	*TID*	*HPLC*
Hand grenade fragment						
Cotton swab	600	630	610	690	88	120
Swiped fragment	190	200	250	310	23	34
Coupons						
Unswiped coupon	850	940	760	920	890	910
Unswiped coupon	890	950	860	930	1000	920
Cotton swab	780	820	620	730	690	720
Swiped coupon	79	78	180	150	140	140
Cotton swab	800	820	700	790	710	710
Swiped coupon	50	51	51	58	60	54

* GC-TID
** Method 8330

Two mortar fins that had been recovered from impact craters following proper detonation were each wiped several times with acetone moistened cotton balls. In each case an area of approximately 16 cm^2 was wiped at various locations (inside and outside of the stem, between one set of tail fins and inside the bottom of the stem) on each of the two fins. After air-drying, each swab was placed in the barrel of a 5-mL plastic syringe, a filter was attached, and 1 mL of acetone was placed on the swab. The plunger was then inserted and the swab was depressed to release the solvent. Table 3 compares the GC-TID and Method 8095 concentration estimates obtained for NG, the only explosive detected, in the acetone extracts.

Table 3. Comparison between GC-TID and Method 8095 for NG in extracts of wipe samples of 120-mm mortar fins.

	NG (mg/L)	
Sample location	*GC-TID*	*Method 8095*
Fin A		
Stem exterior	0.29	0.26
Stem interior	2.3	2.0
Between tail fins	0.12	0.19
Bottom interior	1.2	0.92
Fin B		
Stem exterior	10	11
Stem interior	3.7	2.5
Between tail fins	7.2	4.3
Bottom interior	2.0	1.7
Method blank	0.00	0.0035

Fourteen soil sample extracts were screened using the visual colorimetric method described above, then diluted as needed to achieve analyte concentrations below 50 mg/L prior to GC-TID analysis. Six of the samples were taken from archived soil stored at the Cold Regions Research and Engineering Laboratory, and the remainder were samples (sample splits) that had been used as part of the U.S. Environmental Protection Agency's Environmental Technology Verification (ETV) Program (www.epa.gov/etv). All of these samples were handled so that the colorimetric screening and subsequent GC-TID analysis were blind (sample identity was masked). Table 4 shows the dilutions made based on the colorimetric screening and a comparison between GC-TID and Method 8330 concentration estimates.

Table 4. Sample extract dilutions based on colorimetric screening and comparison between GC-TID and Method 8330 results for the analysis of soil extracts and soil sample replicates. The GC-TID was calibrated over a range of 0.5 to 50 mg/L. Only those analytes with the highest concentrations are presented in the table. Several of these samples also contained 2,4-DNT and TNB, and one contained tetryl.

	Colorimetric screening dilutions		*TNT (mg/kg)*		*RDX (mg/kg)*		*HMX (mg/kg)*	
	1st Spray	*2nd Spray*	*TID*	*HPLC*	*TID*	*HPLC*	*TID*	*HPLC*
Soil sample extracts								
1	1:10*	1:100	690	640	480	517	<120	<30
2	ND**	1:10	<0.5	<0.5	<0.5	<0.5	71	77.9
3	ND	ND	52	51.5	<0.5	0.18	<2.0	<1.5
4	ND	ND	<0.5	0.12	<0.5	0.05	<2.0	<1.0
5	1:10	1:10	630	642	73	53.4	23	37
6	1:1000	1:10	12000	11700	<10	<60	<100	<300
Soil sample splits†								
7	ND	1:10	<0.5	<0.5	<0.5	<0.5	250	180
8	ND	1:10	<0.5	<0.5	<0.5	<0.5	220	210
9	1:1000	ND	18000	23000	<50	<50	<200	<2
10	1:10	1:100	110	120	2100	2300	260	260
11	1:10	1:100	76	76	1000	1100	200	180
12	1:10	ND	81	84	11	7.1	<20	<2
13	ND	ND	1	0.9	100	110	20	15

* Dilution made based on colorimetric screening
**ND – no dilution necessary
† Samples from the Environmental Technology Verification Program. HPLC analysis of sample splits were performed by a reference laboratory.

RESULTS AND DISCUSSION

Tables 2–4 show that there was good agreement between the concentration estimates that were established by the GC-TID method and those determined with either Method 8330 or Method 8095. Past participation in the EPA's Environmental Technology Verification Program (www.epa.gov/etv) and work in a land mine field (Hewitt *et al*., 2001) were also very successful. For example, the on-site method of analysis established more accurate explosive concentrations for reference samples than those obtained by the reference laboratory for the ETV program and allowed us to delineate the surface boundaries of explosives' residues above buried land mines. These two activities highlight the reliability and flexibility of this analytical method.

The recoveries of explosives using a cotton swab moistened with acetone (>70%) from the hand grenade fragment and spiked coupons also agreed with previous trials (Hewitt, 2001). Furthermore, the ratio of RDX to HMX, 7.74, for the Comp B filled hand grenade was in good agreement with a previously established value (7.61) using Method 8330 (Jenkins *et al*., in press). Although the surface wipes of the 120-mm mortar fin failed to detect a distinct distribution of NG, its presence is consistent with earlier efforts. For example, testing of mortar fins for NG when this explosive was present in the igniter has shown that this analyte can remain on surfaces for several years, regardless of its environmental settings (M. Walsh, personal communication, CRREL).

The novelty of this effort involved the coupling of a quick and simple colorimetric screening test with a GC-TID analysis. Pre-screening is advisable for any GC analysis of unknown samples. Indeed, the ability to perform timely on-site GC analyses can easily be confounded by inadvertently introducing a high-concentration sample because of the time involved to return the analytical system response to baseline conditions (i.e., to avoid false positives for subsequent analyses). The findings in Table 4 show that this colorimetric screening test can identify high concentrations of both nitroaromatic and nitramine explosives independently of each other or in the same sample extract. The success of this preliminary study has encouraged us to recommend this technique for use in range characterization activities involving on-site sample analysis.

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DEVELOPMENT AND EVALUATION OF MERCURY CEMS FOR COMBUSTION EMISSIONS MONITORING

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In the United States, mercury (Hg) continuous emission monitors (CEMs) for combustion sources are primarily used as process control monitors and research tools. Hg CEMs are also being considered for emissions compliance assurance applications. However, in order to be considered as a compliance assurance option, measurement performance must be characterized and accepted. Independent research efforts have done much to further the monitoring technology, including improved sample conditioning techniques, minimization of measurement biases and development of quality assurance tools, in addition to laboratory and field testing to evaluate Hg CEM measurement performance. These evaluations have examined the measurement performance of both total and speciated Hg CEMs under a variety of combustion conditions, including coal utility and chlorinated waste combustion. As a result, Hg CEMs have potential application as a process control monitor as well as a compliance assurance tool. The proposed presentation and paper will discuss the current state-of-the-art of Hg monitoring technology, recent performance evaluation/performance demonstration activities and relevant measurement and implementation issues.

THE USE OF ACCELERATED SOLVENT EXTRACTION FOR THE CLEANING AND ELUTION OF XAD RESIN

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XAD resin is used as a solid phase media in the sampling and analysis of air and water for environmental contaminants such as pesticides, PAHs and PCBs. In order to detect these analytes at the required levels, the resin must be extremely clean prior to sampling. Current cleaning methods involve days of extraction using liters of high-quality organic solvents in Soxhlet apparatus. This process adds complexity and cost to analysis. After sampling, large quantities of solvent are used to elute the compounds of interest prior to analysis.

Accelerated solvent extraction (ASE) is now widely used to extract solid samples such as soils, sediments and tissues containing RCRA target analytes. ASE uses conventional liquid organic solvents at elevated temperatures to increase the efficiency of the extraction process. Extractions normally taking hours or days can be done in 15-20 minutes using ASE. US EPA Method 3545A was created in 1995 in order that laboratories involved in environmental analysis could use ASE to improve the efficiency of the extraction process.

Using ASE for the cleaning and elution of XAD resins has numerous advantages over the traditional techniques. Savings in solvent volume and time, while maintaining high recovery levels are significant. There is a concern however that the elevated temperatures used in ASE may alter or destroy the surface of the resin or lead to cracking of the resin bead itself. This presentation will describe the development of an ASE method for the effective cleaning and elution of target compounds from XAD while maintaining the integrity of the resin material.

SAMPLING FOR SELECTED ALDEHYDE AND KETONE EMISSIONS FROM STATIONARY SOURCES

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To ensure that the stack gas collection and analyses of trial burns are conducted in accordance with the approved trial burn plan (TBP), the quality assurance project plan (QAPP) and the standard operating procedures (SOP) identified in various regulatory and guidance documents, comprehensive oversight is conducted by both state and federal regulators.

Stack gas testing was conducted on a liquid and gas burning incinerator designed to burn acrylate liquid wastes. The testing was conducted to show compliance with the 40 Code of Federal Regulations (CFR) Section 264.343. The testing procedure to be described was conducted to demonstrate a Destruction and Removal Efficiency (DRE) of the formaldehyde Principal Organic Hazardous Constituent (POHC) of 99.99% or greater.

The DRE of the formaldehyde POHC was determined by comparing the amount of formaldehyde emitted from the incinerator to the total formaldehyde fed to the incinerator. The inputs for this calculation included all liquid and gaseous waste stream feeds and the additional surrogate spiking.

A high performance liquid chromatography (HPLC) analysis procedure was used to determine the formaldehyde concentrations within the waste feed and stack gas samples in order to determine the DRE of the formaldehyde POHC.

Due to a lack of chromatographic separation between the formaldehyde POHC and an interfering compound, the calculation of the DRE was determined to be negatively biased. Consequently, all DRE testing may have to be repeated.

Lessons Learned:

1. Percentage breakthrough assessment for the interfering compound, between impingers one and two, was undeterminable due to the volumetric carry over from the wet stack gas. Instead, breakthrough was assessed between impingers two and three.

2. Tangent Skim is an ineffectual chromatographic tool when used to separate POHC peaks from interfering compounds, due to the level of bias within measurement.

3. The experimental conditions and chemical equilibria between the POHC and interfering chemical compound must be evaluated for commingling.

4. When manual integration must be performed on POHC peaks of this nature, some bias will be inherent within the area determination.

5. The use of best professional judgement in evaluation of a POHC data set.

INTRINSIC TRACERS AND ENVIRONMENTAL RESTORATION

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Over the last ten years many novel approaches have been developed that use naturally occurring isotopes and other contaminant fingerprinting techniques to understand the fate and transport of contaminants within natural systems. Many more environmental professionals are beginning to use isotopes of carbon, oxygen, hydrogen, sulfur, strontium, boron, chlorine and several others to understand groundwater system recharge, delineate sources of contamination and estimate receptor exposure scenarios. While these isotopes have tremendous potential for helping environmental professionals understand natural and contaminated systems data quality issues are new and challenging. In this presentation some of the potential applications of intrinsic tracers will be examined from three large groundwater programs performed within the U.S. Specific applications of intrinsic tracers that should be included in an environmental professional's bag of tools will be presented. Limitations related to the use of intrinsic tracers that need to be considered prior to selection of tracers will be examined using case studies. Cost benefits and limitations for the most commonly used tracers will be discussed. Until recently intrinsic tracer methods have been used for narrowly focused research efforts. Expanding the application of tracers to environmental restoration projects puts increased pressure on practitioners to modify existing methods such that the level of documentation and data quality match the intended use for the data. Using complementary tracer analyses and traditional forms of geochemical data analysis intrinsic tracers provide an extremely powerful tool in delineating and understanding natural and contaminated systems. Because of the newness of many of the applications practitioners need to team with technology providers to assure that the data collected meet the intended use. Sources of information concerning the use of intrinsic tracers will be provided along with examples of lessons learned.

SUBSURFACE PROFILING SYSTEMS
The use of *Effective Data* for making defensible project decisions

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ABSTRACT

We can no longer afford to rely on limited data sets to make decisions that effect human health and the environment. Continuous subsurface profiling systems are beginning to play a very important role in providing ample amounts of effective data for many site decisions. But clearly a better understanding of the quality of the data generated and its intended use is important.

The Membrane Interface Probe is sensitive to a full range of volatile organic compounds, including chlorinated solvents, petroleum hydrocarbons and methane. This chemical profiling system is combined with an electrical logging tool for characterizing soil type. The combination produces electronic data sets that allows us to quickly observe how the chemicals of concern behave relative to the variations in soil types and hydrologic units. The speed in which this can be observed and then processed is invaluable to the site manager and has made the concept of a dynamic work plan a reality.

Emerging technologies can provide effective data for meeting many site assessment, remediation and monitoring needs. The MIP technology provides real-time, reliable data that is effective for a range of decisions. This technology provides much more data than is obtainable from other methods for a fraction of the cost. If proper protocols are followed the data generated can meet all of the requirements to be considered data of known quality. It is easily processed – right on site - to give you a more complete picture of your site and help you communicate this picture to others.

INTRODUCTION

Over the past 20 years, the successful investigation and remediation of sites has been hampered not only by financial constraints and the technology available at the time, but also by project design and misconceptions about data quality. We may not have much control over the first two of these problems, but we certainly can have control on the second two. Furthermore as faster, better and cheaper technologies emerge, it is even more appropriate to reevaluate project design and data quality objectives to ensure that optimal use is made of technology innovations.

One area where technology is advancing is in our ability to obtain better and more complete information of physical and chemical conditions in the subsurface. We need to fully understand the type of data these emerging systems produce in order to best incorporate them into site assessments, remedial design and performance monitoring efforts. In this paper I will preface remarks about Subsurface Profiling Systems with a few comments on the types of data needed for site investigation and remediation tasks.

EFFECTIVE DATA

Since the subsurface is heterogeneous, it is difficult to understand the details of the fate and migration of chemicals that we introduce into it. Typically, we use soil borings and monitoring wells in our attempts to describe the variations in soil type and water flow. We then obtain samples from a limited number of locations for "definitive analysis" in a laboratory that has been certified by the State to ensure that we get "high quality" data. What do these terms mean? Are they relevant? Is this the best way to spend limited resources?

The cost of this process is high and often results in too few data points to fully understand subsurface conditions. As a result, wrong conclusions are reached, inappropriate decisions are made and subsequent activity reveals these errors, requiring remobilization and ongoing investigations. Unfortunately, the follow up investigations typically follow the same approach and produce the same inappropriate results. If this occurs, we have failed in our responsibility to investigate and communicate the health risks and environmental problems associated with the site.

This approach has risen out of a perceived need to have high quality, definitive, "laboratory data". Most investigators and regulators are more comfortable with laboratory data than with "screening data." There is a general perception that data, generated in a certified laboratory, following an established EPA Method provides a reliable basis for making decisions about site conditions. This is certainly an oversimplification and in many cases just not true.

The method used and the location where the sample is analyzed is simply not relevant to most of the important decisions that need to be made during an investigation. All the effort required for assessing the analytical error of a single sample is not as important as the overall decision errors that can be produced by a fixation on laboratory data. The major source of uncertainty in site investigations (as much as 90%) is sampling variability due to the heterogeneity of environmental matrices. *Therefore the primary measure of data quality is whether the sample is representative of the area being evaluated.*

The goal of most site assessment work is to build this picture. Our focus should be on understanding the site and collecting sufficient data of known quality to fully understand:

- the lithology and hydrology of the site;
- the nature and extent of the chemicals of concern in the source area, the vadose zone and the saturated zone; and
- how lab results from a limited number of samples can be extrapolated throughout the site.

The focus of a project design should be to determine how much data is needed to establish a detailed picture/understanding of the subsurface and to pick technologies that can produce data of known quality for building this picture. None of the data for building this picture needs to come from a laboratory. Deana Crumbling of the USEPA calls this type of data Effective Data. It is data of known quality that is effective for meeting the intended purpose of the investigation.

Once this is accomplished, then there may be a regulatory requirement to get laboratory results on selected parts of the picture to determine how it compares to regulatory standards.

But this should not automatically be assumed to be required.

So in assessing emerging technologies we are interested in ones that can supply us with data that are effective for achieving our stated project goals. It is possible that a project's goals can be met solely with effective data during the investigation, remediation and even the monitoring phases. If they can, then all of the opportunities for introducing error into the chain of events leading up to an acceptable laboratory result can be avoided.

THE ULTIMATE TOOL – *A Continuous Chemical Profiler*

One elusive goal of the environmental industry over the past 15 years is to produce a tool that will provide continuous chemical data in real time as it is pushed into the ground. Such a mythical tool would remove most of the sampling errors inherent in traditional approaches, because it would produce copious amounts of continuous chemical data *in situ*. If samples were still required to be sent to a laboratory for verification purposes, there would be a much higher confidence that they were representative of "something" since their selection would be based on a much more continuous and complete picture of the subsurface than previously available.

CURRENT CHEMCIAL PROFILING SYSTEMS

The mythical, continuous, chemical profiler that gives lab quality data on all chemicals of concern does not exist. However, there have been several noble attempts at achieving this goal, at least for several suites of compounds. Two commercially available approaches are the Laser Induced Fluorescence (LIF) system and the Membrane Interface Probe (MIP) system.

The LIF system is based on identification of compounds that fluoresce, principally the heavier petroleum compounds. A light is sent out through a sapphire window on the side of a downhole tool and it excites compounds that come into contact with the window. Naturally occurring organic matter and petroleum hydrocarbons will fluoresce and this signal is picked up by the tool and processed in order to identify the organic compound present. The LIF system is a good tool for locating free phase hydrocarbons but is not generally sensitive to the light-end hydrocarbons such as BTEX. The tool works well for free product in the vadose zone. It commonly does not "see" dissolved phase constituents because there is not enough material presented to the window of the probe. Chlorinated compounds don't fluoresce well and thus the tool is not appropriate for solvent sites unless a high petroleum content is dissolved in them.

The MIP system, in contrast to the LIF system, is sensitive to a full range of volatile organic compounds, including chlorinated solvents, petroleum hydrocarbons and methane. The chemical profiling system is combined with an electrical logging tool for characterizing soil type. The combination produces electronic data sets that allows us to quickly observe how the chemicals of concern behave relative to the variations in soil types and hydrologic units. The speed in which this can be observed and then processed is invaluable to the site manager and has made the concept of a dynamic work plan a reality. The essential parts of a MIP system are:

- **Electrical Conductivity -** The Wenner Array on the MIP system provides a reasonable estimate of the electrical conductivity of the soil/water layers that it passes through.

Grain size is the dominant variable of the electrical conductivity in soils. Coarser grained sediments, such as sands, have lower conductivity. Finer grained sediments such as silts and clays have higher conductivity. The chemical constituents in the groundwater can also affect conductivity. Salts raise the electrical conductivity of water, so brine horizons will have a higher background than fresh water aquifers.

- **The VOC sampling system -** The essence of the VOC detection system is a teflon coated membrane, set within a heating block, on the side of the Direct Push tool. The soils and water that come in contact with this block are quickly heated to 120 degrees C. Chemicals with lower boiling points are volatilized and diffuse across the membrane and into a sampling loop via chemical and pressure gradients. The VOC gases are then carried to various detectors at the surface in an inert carrier gas. This system is not effective for most semi-volatiles, metals or radioactive compounds. The temperature varies as a function of penetration rate and the thermal properties of the materials through which it passes. A temperature log can be used to locate the groundwater table and water rich units, since they tend to cool the probe down more quickly than just changes in soil type.
- **Analysis of the VOCs -** There is a choice as to how the VOCs are analyzed once they get to the surface depending on how the specific MIP system deployed is set up. The most common and effective approach is to use a continuous monitoring detector. These detectors yield a milli-volt response for the whole suite of compounds that they are sensitive to, for example, an electron capture detector (ECD) responds just to the chlorinated solvents, the photo ionization detector responds best to the aromatic hydrocarbons, the flame ionization detector (FID) responds to methane and other petroleum hydrocarbons. Speciation of discrete samples is also possible. However for many applications, reliable data on the precise depth and relative concentration is adequate for many decisions.

INTENDED USE OF DATA

Subsurface Profiling Systems such as the MIP can be used as an integral part in investigations, remediation and in monitoring. In many cases, depending on the planned use of the data, the results generated may be fully adequate to meet all of your project needs. In fact, in a typical MIP day, hundreds of feet of logging can be performed, the electronic output dumped into a laptop and both chemical and physical data fully processed together to show if adequate information has been gathered to meet the project objectives. This is a very powerful tool and provides a much more compete data set than previously available. It can be used for:

- documenting the soil/sediment/saprolite stratigraphy of the site,
- delineating the source, migration pathways and extent of chemicals of concern,
- targeting locations for collecting representative samples from wells, borings or DPT,
- providing the framework for extrapolating analytical results,
- identifying hydrologic/contaminated zones for focused treatment,
- targeting optimal locations for installation of a monitoring system,
- providing baseline conditions for a monitoring system, and
- dynamic monitoring of system performance or plume migration.

DATA QUALITY MANAGEMENT

In order to use MIP results as effective data, the data it produces should be of known quality.

However, we must also realize that we are dealing with a continuum of data, not a single sample that should follow the traditional laboratory QAQC protocols. The supplier should have a Quality Assurance Plan that documents what quality control procedures need to be in place. A few of the important steps that should be followed to ensure that the results are of known quality are listed here:

- To verify that the electric logs are identifying the key soil types, at least one continuous core should be collected and correlated with the logs for each geologic regime encountered.
- To determine the appropriate spacing for a MIP survey, the conductivity and chemical logs should be processed together and plotted in a transect across the site. They should then be examined for continuity of features that may be significant to the fate and migration of the chemicals of concern. Any large disconformity between profiling locations can then be filled in with an additional MIP log.
- To ensure consistency in volatilization of VOCs, probe penetration should be halted if temperatures fall below 100 degrees, until the probe temperature has recovered to optimum operating range.
- To verify the integrity of the membrane, transfer line and detectors, a response check for a reference standard should be conducted prior to each run and the mass flow rates/line pressures monitored to check for clogging and leakage.
- To determine the sensitivity of each detector for a particular analyte, a range of known concentrations of the selected chemicals of interest should be tested in the laboratory.
- To speciate and quantitate responses on the MIPs, discrete samples should be collected and analyzed via GC or GCMS.

COST ANALYSIS

When comparing the costs for characterizing sites with conventional approaches versus using subsurface profiling technologies, there are several aspects to be considered:

- **Initial Assessment Costs** – For the same basic scope of work, i.e., number of locations, depths and analysis, MIP surveys cost less in the majority of cases.
- **Need for Repeat Visits to the Site** – Due to the completeness of information gathered on a site with a MIP survey, it is far less likely to have to remobilize to the site to collect additional data.
- **Need for Remediation** – Since the MIP survey provides a more complete picture of the contamination and subsurface conditions, it has resulted in a better understanding of the potential risks. With this knowledge, many sites may not have to be remediated.
- **Remediation Costs** – Excavation or treatment costs are often more limited since the detailed information provided by a MIP survey allows more surgical applications of the selected treatment approach.
- **Monitoring Costs** – With a more complete picture of the subsurface, fewer wells may be necessary for monitoring purposes. Periodic MIP surveys may be able to replace the need for wells completely.

SUMMARY

The need to use effective data as the primary source of information on site investigations is great. We can no longer afford to rely on limited data sets to make decisions that effect human health and the environment. Continuous subsurface profiling systems can play a very important role in providing ample amounts of effective data for many site objectives. But

clearly a better understanding of the quality of the data generated and its intended use is important.

To avoid the misuse of this type of data, one must recognize the need for good comprehensive QA/QC to limit the overall project error. This should include the incorporation of experienced operators in the planning and interpretation phases of the project in addition to the field operations. If this is not done, then we will not optimize the use of this promising technology and possibly fall back into the same predicament of many conventional investigations – trying to make decisions with too few data points or with data of unknown quality.

The successful use of the MIP technology requires a combination of:

- well maintained equipment,
- operators experienced in operating, maintaining and problem solving,
- proper project design to ensure that any sample acquired is representative of a well-defined part of the site,
- proper QA/QC to ensure that the data are of known quality,
- the appropriate analytical detectors for the compounds of interest, and
- the capability to create transects of the site in order to check for adequate spacing.

These abilities are often best obtained by partnering with those entities who can assist in the planning, performance, delivery and QA review of the data to ensure it is acceptable.

Emerging technologies can provide effective data for meeting many site assessment, remediation and monitoring needs. The MIP technology provides real-time, reliable data that is effective for a range of decisions - that can be made right on site. This technology can provide much more data than obtainable from other methods for a fraction of the cost. If proper protocols are followed the data generated can meet all of the requirements to be considered data of known quality. It is easily processed - right on site - to give you a more complete picture of your site and help you communicate this picture to others.

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GETTING TO THE BOTTOM LINE: DATA QUALITY VS DECISION QUALITY

D. Crumbling

No abstract available.

A SIMPLE APPROACH FOR ASSESSING DATA QUALITY UNDER A PERFORMANCE-BASED MEASUREMENT SYSTEM

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ABSTRACT

Because reliable matrix-specific control limits are not available to evaluate laboratory performance prior to contract award and sample analysis, a simple approach is proposed for assessing laboratory performance and data quality under a Performance-Based Measurement System (PBMS). The proposed approach compares performance data with project-specific Method Quality Objectives (DQOs) before selecting a laboratory for sample analysis. The approach emphasizes the use of four key quality assurance/quality control (QA/QC) elements: standard operating procedures (SOPs), Method Detection Limits (MDLs), laboratory control samples (LCSs), and proficiency testing. A laboratory must establish and implement detailed SOPs for all major operations, and demonstrate its performance by MDL studies, LCS analysis and frequent proficiency testing with blind real-world performance evaluation (PE) samples. These four elements are deemed as the basic minimum needed for a laboratory to establish and demonstrate its performance and data quality. Data generated and reported under the proposed approach meet the reporting requirements of the new International Organization of Standardization (ISO) Standard 17025.

INTRODUCTION

The production of data of known and acceptable quality that meet project-specified DQOs is a primary goal of every environmental sampling and analysis activity. USEPA's Environmental Monitoring Management Council (EMMC) recommends using PBMS for environmental sample analysis. EMMC defines PBMS as "A set of processes wherein the data quality needs, mandates or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those needs in a cost-effective manner." To determine data quality needs, USEPA developed a seven-step DQO process that provides project-specific limits on decision errors. Based on data quality needs, data users or accrediting authorities determine if a laboratory is qualified to perform sample analysis prior to a contract award and if the data produced are of acceptable quality afterwards.

It has been observed that the data quality in many environmental data packages is often unknown or not well defined. Typical data packages contain analyte concentrations for all detections, "ND" or "<" symbols and quantitation/reporting limits for non-detects, and associated quality control (QC) results and acceptance limits. The QC data usually include the analytical results of calibration verification samples, blank samples, LCSs, matrix duplicates (MD), matrix spikes (MS) and matrix spike duplicates (MSD), depending on the contract's specifications. However, these QC data do not necessarily reflect the quality of associated sample results because of errors or ambiguities associated with the quantitation/reporting and

QC limits or the improper use of matrix-specific QC samples.[1] As a consequence, data of so called "known quality" often cannot be compared with action levels for reliable decision making.

The proposed approach places less emphasis upon matrix-specific QC samples such as MD, MS and MSD. This is because environmental chemical testing laboratories generally do not possess reliable matrix-specific control limits. Twenty samples of "similar" physical composition are usually grouped into one batch and one or two samples are selected for the MD or MS/MSD analyses. While the MD and MS/MSD samples might have been taken from the same site, the sample might vary greatly in physical composition (e.g., clay versus sandy soils or different organic content). Furthermore, a laboratory often pools MD or MS/MSD data of similar matrices from different sites or projects to establish matrix spike control limits. The control limits derived from these matrices can be very wide (e.g., due to the wide variations in sample composition) and are not typically representative of the actual laboratory performance on a site-specific matrix. This is a significant problem, especially for soil samples. Because of the heterogeneous nature of soil samples, in order to generate reliable control limits for matrix-specific QC samples, a laboratory needs to run 20 to 30 matrix spiked samples of the same matrix to establish initial control limits. But most environmental measurement projects do not require or pay for establishing project and site and matrix-specific control limits.

This article presents a simple approach for evaluating laboratory performance and data quality. The approach is based upon existing strategies that have been adopted by most environmental laboratories, and is applicable to both definitive and screening methods. The approach does not require any major, new or additional QA/QC data or information to be generated but uses existing laboratory QC information. The approach uses four key laboratory QA/QC elements – SOP, MDL, LCS and PE samples – which are proposed as the minimum elements needed to establish and demonstrate laboratory performance and data quality. Although both sampling and analysis errors affect the quality of environmental data, the following discussions focus on laboratory analytical errors (i.e., precision and bias). There is no simple or cost-effective procedure to evaluate data quality based on matrix-specific QC data. The proposed approach is an alternative that is believed to be simple and easy to implement (i.e., will not entail major changes to the existing laboratory QA/QC procedures or incur significant increases in analytical cost). In general, in the context of the evaluation of overall method performance, an underlying assumption for the approach is that a "better" laboratory will have lower MDLs and tighter control limits for LCS recoveries. (Note that this does not mean that tight QC limits must be used for all projects; it is being noted, given a variety of projects, tight QC limits will potentially satisfy a greater number of DQOs.)

THE PROPOSED APPROACH

The proposed approach emphasizes four key elements of conventional laboratory QA/QC operations:

- SOP Preparation
- MDL Study
- LCS Analysis
- Proficiency Testing

First, a laboratory should follow USEPA QA/G6, "Guidance for Preparing Standard Operating Procedures (SOPs)," to prepare detailed SOPs for all key laboratory operations that affect data quality and document the results of key operations.[2] The SOPs and documentation provide an important aspect of scientific evidence and legal defensibility for reported data.

Second, a laboratory should follow 40 *Code of Federal Regulations* (CFR) 136, Appendix B to establish MDLs for all target analytes. MDLs should be method-specific (e.g., be specific to both the preparatory and determinative methods of analysis). If all laboratories use the same procedure to determine MDLs, the MDLs would be a good universal indicator for the evaluation of laboratory performance. Based on MDLs, a laboratory determines the method quantitation limits (MQLs) and the concentration of the lowest, allowable calibration standards. The uncertainty of analytical data increases as analyte concentrations decrease and approach the MDLs. At the 95% confidence level, the estimated relative uncertainty for analytes measured at a concentration of *N* times MDL is approximately:

$$\pm \frac{2\sqrt{2}\ x\ 100}{N\ x\ t_{(n-1,\ 0.99)}}\%$$

(1)

where $t_{(n\text{-}1,\ 0.99)}$ is the Student's *t* factor for the 99% confidence level and *n*-1 degrees of freedom (where *n* is the number of replicates analyzed for the MDL study).[3] At the MDL, the relative uncertainty would be about ± 100% with 95% confidence. At concentrations greater than the quantitation limit, the estimated relative uncertainty is determined from LCS recovery data (to be discussed next). Because of the large uncertainty near the MDL, information regarding analytical bias at concentrations less than MQL is not readily available and is assumed to be equal to the bias for the LCS recoveries.

Third, a laboratory should follow a uniform set of protocols (to be discussed later) to establish control limits for the recoveries of LCSs (i.e., blank spikes). If all laboratories follow the same protocols to establish control limits for LCSs, empirically established in-house control limits would be another good universal indicator for laboratory performance and data quality. Because LCSs are prepared from clean matrices (e.g., reagent water and purified sand), LCS results provide only lower bound limits for the total measurement uncertainty associated with field samples. The relative uncertainty of the bias-corrected mean recovery for field samples could be estimated as follows:

$$\pm \frac{t_{(n\bullet 1,\ 1\bullet a/2)}\ x\ s_{\ LCS}\ x\ 100}{\%R}\%$$

(2)

where $t_{(n\text{-}1,\ 1\text{-}a/2)}$ is the Student's *t* factor with *n*-1 degrees of freedom at (1 - a/2) × 100% confidence level; σ_{LCS} is the standard deviation of the percent LCS recovery; and %*R* is the mean LCS recovery.[4,5] The mean LCS recovery is assumed to provide a measure of bias for samples at concentrations greater than MQLs (i.e, rather than the mean MS recovery because representative MS data are typically not available).

Last, because LCSs are prepared with interference-free matrices, laboratory performance on LCSs may not reflect the laboratory performance on actual field samples, which typically have more complicated matrices. (Unfortunately, matrix-specific QC samples such as MD, MS or MSD usually do not provide much useful information because of dissimilarities between the matrix-specific QC samples and the other field samples in a batch as well as the samples used to establish the laboratory's "matrix-specific" control limits.[1]) In addition, laboratory performance on field samples also depends upon the laboratory's ability to select and perform additional matrix-specific sample preparation and/or analysis procedures such as extract cleanups, matrix modifications, method of standard additions, etc. Frequent proficiency testing with blind real-world PE samples is an excellent way to test laboratory performance on actual field samples. Double blind PE samples are preferred to single blind PE samples. If a laboratory is able to pass double blind PE samples on a routine basis, the laboratory has demonstrated its performance on analysis of actual field samples.

These four elements form the foundation for the proposed approach. In order to use this approach to evaluate laboratory performance or data quality, at a minimum, one must request the laboratory to report: MDLs; dilution factors; and spike concentrations, recoveries, and in-house control limits of LCSs. When using MDL studies and LCS recoveries to assess laboratory performance and data quality, consistency and comparability among different laboratories are assumed. The procedures used to determine MDLs and the control limits for LCS recoveries will affect the values of MDLs and control limits, and hence the uncertainty estimates. It should be noted that many laboratories do not follow 40 CFR 136 (to determine MDLs) exactly as the procedure is written and use different procedures to establish LCS control limits. The remaining discussions address those variations and propose standardized protocols for determining MDLs and LCS control limits.

SOP PREPARATION

ASTM D 5172-91 (1999) states:

> *A significant part of the variability of results generated by different laboratories analyzing the same samples and citing the same general reference is due to differences in the way the analytical test methods and procedures are actually performed in each laboratory. These differences are often caused by the slight changes or adjustments allowed by the general reference, but that can affect the final results.*

Well-written SOPs can minimize such differences. According to USEPA guidance document QA/G6, an SOP is intended to be specific to the organization or facility whose activities are described. If an SOP is written for a standard analytical method, the SOP should specify analytical procedures in greater detail than in the published method to ensure that the procedure is performed in a uniform, reliable and reproducible fashion within the organization. An SOP delineates the specific procedures used to carry out a method and how (if at all) the SOP differs from the standard method. An SOP, at a minimum, should contain a high level of detail.

By reviewing detailed SOPs, the reviewer can readily determine how a laboratory performs MDL studies and whether LCS analyses are performed using the same protocols used by other laboratories. MDL and LCS data, like the SOPs, are available for laboratory

performance and data quality assessments prior to contract awards and after analysis begins.

MDL STUDY AND USAGE

Although most laboratories follow Appendix B of 40 CFR 136 to determine MDLs, there are some variations, which may affect the reported values of the MDLs. According to 40 CFR 136, the procedure involves spiking seven replicate aliquots of reagent water or sample matrix with analytes of interest at a concentration within one to five times the estimated MDLs. The seven aliquots are carried through the entire analytical process; the standard deviation of the seven replicate analyses is calculated; and the MDLs are the products of the standard deviations and the one-tailed Student's *t* factor for *n*-1 degree of freedom at 99% confidence level.

However, when MDL studies are performed, laboratories often use inappropriately high spiking concentrations, which often results in inaccurate MDLs (e.g., low-biased MDLs). According to Appendix B of 40 CFR 136, the spike concentrations of the seven MDL spikes should be one to five times the estimated MDLs for reagent water matrix and one to ten for clean solids or sample matrices. Otherwise, the spike concentrations are adjusted and the study repeated until the ratios are within these ranges. Because MDLs are based on the variances at the measured concentrations, the validity of the ratios between spike concentration and estimated MDLs should be verified by comparing the mean of the seven measured concentrations, instead of the nominal spike concentration, with the calculated MDLs.

The validity of the MDLs should be verified on a routine basis or after each major instrument maintenance. Based on the definition of the MDL presented in 40 CFR 136, there is a 1% probability that a sample with no analyte will produce a concentration greater than or equal to the MDL. However, there is a 50% probability that a sample with a true concentration at the MDL will be measured as less than the MDL or a non-detect. For this reason, the validity of the calculated MDLs should be checked with MDL check samples spiked at the Reliable Detection Limits (RDLs).[6] There is only 1% probability of a false negative (i.e., a non-detect) at the RDL, which is equal to about two times the MDL. MDL check samples should be taken through the same process used initially to establish the MDLs. If a laboratory can detect the MDL check sample, the validity of the MDL is verified.

A laboratory should establish its MQLs based on its MDLs. At the MQLs, the analytical uncertainties should be approximately equal to the uncertainties for the LCS recoveries (typically, ± 10 – 30%) or no less than the calibration uncertainties, which are equal to the method specified acceptance criteria for initial calibration verification (ICV) or continuing calibration verification (CCV). The acceptance criteria for ICV/CCV are usually ± 10% for inorganic (e.g., metals and anions) and ± 20% for organic analyses. MQLs should therefore be set at about ten times the MDLs for inorganic analyses and five times the MDLs for organic analyses. MQLs also determine the concentration of the lowest calibration standard.

Because of the large uncertainty and bias associated with measured concentrations near the MDL, the USEPA did not specify acceptable limits for analyte recoveries for MDL studies. However, if there is an excessively low or high recovery, the MDLs may not be meaningful and an MDL check sample should be used to verify or estimate the MDL. For example, an MDL of 5 µg/L based on 100 µg/L MDL spikes and 10% recoveries is not acceptable, because one

could not reliably detect a 10 µg/L spike if the recovery is only 10%.

CONTROL LIMITS OF LCS RECOVERY

Laboratories are often required to meet project-specified acceptance limits for LCSs. The LCS is acceptable if the recoveries of all the analytes fall within the project-specified recovery limits. A laboratory should use statistical control limits that are established based on in-house control charts to demonstrate that methods are under statistical control at a specified confidence level. The 99% prediction intervals for individual future data are typically used as the control limits if certain statistical assumptions (e.g., independent data, normal distribution, etc.) are met.[7] The control limits reported in a data package could be based on contract or regulatory requirements, published method performance data or laboratory in-house empirically established control limits. However, using these control limits is acceptable only if the laboratory has demonstrated its ability to achieve the limits on a routine basis.

When one or more analyte recoveries fall outside of LCS acceptance limits, laboratories frequently reprocess the LCS until all the recoveries fall within the project-specified limits. However, the laboratories' in-house 3-sigma control limits are frequently wider than the project-specified acceptance limits. Under these circumstances, meeting the project-specified LCS acceptance limits via reanalyses of the control samples, does not demonstrate the project Method Quality Objectives are being met. When analyzed in this manner, the LCSs would not be representative of the method precision and bias for the actual environmental samples, since all the LCS recoveries will eventually be within the acceptance limits simply because of random chance. This strategy overestimates the quality of the data. Wider in-house control limits could be due to a small number of LCS recovery data, which often fail to meet statistical assumptions (i.e., normal distribution, independency, etc.). Slightly wider in-house control limits are anticipated and acceptable if the sample size is small; however, when more data points (e.g., $\geq$ 20) are available, the data should show a central tendency and empirically established in-house control limits should meet project-specified control limits as a proof of acceptable laboratory performance.

It is often observed that laboratories establish control limits for LCS recoveries based on three times standard deviations of mean LCS recoveries without consideration of sample sizes, distributions or adequacy of test statistics. Some laboratories establish control limits based on a small number of data points (e.g., <10), while some laboratories establish control limits using several thousand data points collected over an extended time period of several years. A few data points will not provide reliable control limits as discussed above; however, using data points over a very long time period may not present current laboratory performance either. In addition, many laboratories retain only acceptable LCS recovery data for control chart analysis and maintenance so that the control limits are tightened over time. As a consequence, these laboratories have to reprocess LCSs frequently and the reported control limits are not representative of laboratory's actual performance. Out-of-control data could represent true extreme values of a distribution and indicate more variability of the data than expected. The decision to discard out-of-control data should be based on some scientific rationale or quality assurance basis.

Obviously, a protocol for establishing and using control limits is needed to ensure the consistency and comparability of control limits for LCS recoveries among laboratories. The

protocol should address the requirements for the number of analytes, spiking concentrations, matrices used to prepare the LCSs, sample size and distribution, outlier testing and treatment, control chart maintenance and usage, etc. It is recommended that the protocols be established based on ASTM or ISO standards. The proposed approach recommends that each data package contain MDL and LCS control limits for uncertainty assessments by data users. Because LCS limits are based on clean matrices (and field sampling error is not included), uncertainties based on LCS recoveries would represent the "minimal uncertainties." A more complete assessment of the uncertainty of field samples would include sampling errors of the field samples as well as aliquoting and spiking errors in the laboratory as part of sample preparation that are not included in LCS sample preparation and analysis.

The Department of Defense Environmental Data Quality Workgroup (DOD EDQW) is conducting a study to establish standardized DOD-wide method-specific acceptance limits for LCS recoveries. These limits will be used to identify quantitative target windows that laboratories supporting DOD environmental programs will be expected to achieve. Laboratories who would like to contribute data should consult the data collection instructions provided on both the DENIX (www.denix.osd.mil) and the ACIL (www.acil.org) web sites.

PROFICIENCY TESTING

Matrix-specific QC data could be used to evaluate laboratory performance, if reliable control limits are available. But if not, a "real-world" PE sample is just like a matrix spike sample, with well-defined acceptance criteria. Laboratory performance on project samples is frequently evaluated with real-world PE samples of various matrices before and after contract awards. Laboratories whose clients authorize the use of PBMS may select various options among sample preparation, cleanup or matrix modification procedures, based on sample matrices, interferences and laboratory expertise or available equipment. If a laboratory can demonstrate acceptable performance in control matrices (i.e., reagent water and clean solids) and passes real-world PE samples on a routine basis, the presumption is that the laboratory can perform proper sample preparation procedures for specific sample matrices. To avoid potential special treatments for PE samples by laboratories, double blind real-world PE samples with both sample identities and compositions unknown to laboratories are preferred to single blind PE samples.

EXAMPLES

Two examples are presented below to illustrate how to estimate data uncertainty and assess laboratory performance using project DQOs.

1. Data Uncertainty:

If a laboratory has an MDL of 10 ppb and LCS control limits of 72 – 108% and reports 200 ppb for lead in a soil sample, what is the uncertainty of the reported value at 95% confidence level?

The MQL should be about ten times greater than the MDL (i.e., 100 ppb) for metal analysis. Since the reported value of 200 ppb is greater than the MQL, Equation 2 can be used to estimate the uncertainty. Based on the LCS control limits of 90 ± 18%, the relative standard deviation of the mean LCS recovery, σ_{LCS}, is 6% (i.e., 18% divided by three). The estimated 95% uncertainty is:

$$\pm (2 \times 6 \times 100 / 90)\% = \pm 13\%.$$

The true lead concentration could be about 222 ± 30 ppb.

Total uncertainty includes both field and laboratory uncertainties, but the estimated uncertainty in the above example does not include field uncertainties (e.g., sampling errors arising from the inhomogeneity of soils). However, if Pierre Gy's sampling practice is followed, the field uncertainty is about the same magnitude as the laboratory uncertainty, i.e., the total uncertainty would be approximately equal to two times the laboratory uncertainty (i.e., ±60 ppb).[8]

2. Laboratory Performance:
If a project action level for an organic compound in soil is 20 ppb and the acceptable decision errors are $\alpha = \beta = 0.05$, is a laboratory with an MDL of 2 ppb and LCS control limits of 85 – 115% (i.e., $\sigma_{LCS} = 5\%$) acceptable?

In order to ensure that analyte concentrations do not exceed the action level with decision errors $\alpha = \beta = 0.05$, a laboratory should be able to reliably analyze the organic compound at a critical concentration that is no less than $(1 - 8 \times \sigma_{LCS})$ times the action level. (The "8" accounts for the acceptable decision errors of $\alpha = \beta = 0.05$ and the estimated field error.) Based on action level of 20 ppb, acceptance errors of $\alpha = \beta = 0.05$, and standard deviation of LCS recovery (σ_{LCS}) of 5%, the critical concentration is: $(1-8 \times 5\%) \times 20$ ppb or 12 ppb. Because the critical concentration, 12 ppb, is greater than the laboratory's MQL of 10 ppb (i.e., 5 times MDL for organic analyses), the laboratory performance is acceptable.

However, if the LCS control limits are increased to 70 – 130% (i.e., $\sigma_{LCS} = 10\%$), the critical concentration would be equal to $(1 - 8 \times 10\%) \times 20$ ppb or 4 ppb, which is less than the MQL of 10 ppb. The laboratory will no longer be able to reliably analyze the target analyte at the critical concentration of 4 ppb. The laboratory performance is therefore not acceptable for the project. The laboratory should improve its performance to decrease its MDL and/or narrow its LCS control ranges, or perform replicate analyses to reduce the uncertainty. Otherwise, a different laboratory or method with better performance or a different sampling approach (e.g., multiple samples) is needed to meet the project's DQOs.

SUMMARY

Because of their availability, MDL and LCS recovery data could be used as universal indicators for evaluation of laboratory performance and data quality. The precision and bias of LCSs that are determined based on control charts of LCS recovery data can be used to estimate the precision and bias of sample data, and meet the ISO 17025 reporting requirements on estimating uncertainties of measurements. However, to ensure data comparability, laboratories must explicitly follow the same protocols to determine MDLs and control limits for LCS recoveries. Laboratories should frequently run MDL check samples and participate in proficiency testing with double blind PE samples to check the validity of MDLs and laboratory performance on field samples, respectively. Laboratories must prepare and implement detailed SOPs for all key operations and document the results. In-house SOPs on control charts and empirically established LCS control limits should be submitted for review of

laboratory performance before a contract award or sample analysis.

The proposed approach requests no major, new or additional QA/QC and is simple and inexpensive to implement for assessing laboratory performance and data quality. Currently, the U.S. Army Corps of Engineers is evaluating the proposed approach and the initial findings show that acceptable laboratory performance and data quality are strongly correlated with these four QA/QC elements. Other potential users include: accrediting authorities can evaluate laboratory capability and performance prior to a contract award; laboratories could estimate data uncertainties and verify that performance requirements are met; and data users can monitor laboratory performance with LCS control charts and real-world PE samples on a routine basis during the project, and determine data uncertainties based on MDL values and LCS limits.

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MQOS AND MEASUREMENT UNCERTAINTY

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Abstract
Inherent variability of an environmental study population and measurement uncertainties affect the uncertainty in making environmental decisions. Estimation of both study population variability and measurement uncertainties is needed to achieve acceptable total study uncertainty goals.

Controlling various sources of sampling and testing uncertainties ensures that data of known quality are generated because quality data are required for making environmental cleanup decisions.

Measurement Quality Objectives (MQOs) are used to control measurement uncertainty. MQOs are designed to control various phases of the measurement process and to ensure that measurement uncertainty is within an acceptable range for environmental data users.

Measurement Quality Objectives are not Data Quality Objectives (DQOs) or Data Quality Indicators (DQIs). MQOs are project-specific measurement goals derived from DQOs and MQOs are used to achieve DQOs. MQOs are the acceptance criteria or target values for Data Quality Indicators (DQIs).

Examples of DQIs include:
- Detection Limit/Quantitation Limit
- Precision
- Accuracy
- Representativeness
- Completeness
- Comparability

Examples of DQOs include:
- Determine to a 95% confidence level whether or not the concentration of lead in study population soil is greater than 500 mg/kg.
- Determine whether or not the lead concentration at a study population soil poses a human exposure risk.

Examples of MQOs include:
- Reporting limit of 10 mg/kg
- Percent recovery of 80 – 120%
- Relative percent difference of +/-20%
- Measurement variability less than 1/3 inherent variability of study population
- 90% of planned data complete

A systematic project planning, design, implementation, and evaluation program is required to

achieve MQO targets.

Introduction

Data Quality Objectives (DQOs) are the drivers in the Measurement Quality Objectives (MQOs) development process. The DQOs process requires estimation of total study variability or uncertainty. Total study uncertainty is a combination of the inherent population variability of the study contaminant and the measurement variability or uncertainty. Estimation of both the study population variability and measurement uncertainty of contaminants is needed to determine the confidence in the estimate of the total study uncertainty. The measurement uncertainty is a combination of the measurement variability derived from the sampling strategy design, field sample collection, and laboratory preparation and testing. Each tier of the measurement process compounds the total study uncertainty.

Measurement variability "confounds" the estimation of the inherent population variability of the study contaminant. Natural or inherent variability is the fluctuation of the contaminant in the population media that is sampled. Collecting additional samples reduces the uncertainty associated with the average contaminant concentration of the study population. Measurement uncertainty is the difference between the actual population contaminant levels and the sample results. Sampling design uncertainty results because only a limited number of the possible locations that make up the study population are actually sampled and tested. Sample collection variability is affected by the process of obtaining representative samples of a subset of the study population. The subsampling, extraction, separation, concentration, and testing procedures affect laboratory preparation and test determination variability. Selecting appropriate sampling and testing strategies and methods reduces the uncertainty associated with measurement results.

MQOs are designed to control various phases of the measurement process and to ensure that the total study uncertainty is within the prescribed quality levels. Therefore MQOs are used to evaluate the degree of acceptability of the data. MQOs establish acceptable levels of uncertainty for each measurement process. They specify "what" the levels of data performance must achieve, but do not specify "how" those levels of data performance will be achieved. Different approaches to sampling design, sample collection, preparation, and test determination are selected to achieve a specified performance level. MQOs are divided into quantitative and qualitative groups.

Quantitative MQOs include:

- Detection Limit/Quantitation Limit
- Precision
- Accuracy

Qualitative MQOs include:

- Representativeness
- Completeness
- Comparability

Quantitative MQOs

Quantitative MQOs specify the detection limit and quantitation limit that must be achieved for

a particular project. Other quantitative MQOs are precision and accuracy. The Method Detection Limit (MDL) is the low-range analyte concentration that the matrix-specific procedure can reliably detect. Below the MDL, test results are attributable to background "noise" and the relative uncertainty at the detection limit may be considered to be 100% at the 95% confidence level. The Practical Quantitation Limit (PQL) is the lowest analyte concentration that can be determined with known precision and accuracy using a specific procedure for a particular sample matrix.

The MQO for precision must specify how much variability or uncertainty for the measurement is acceptable. Precision is the degree of agreement among replicate measurements while accuracy is a combination of precision and bias (systematic error), and accuracy is the degree of agreement between a test determination (or an average of test results) with the actual amount in the sample. Precision is calculated as the relative percent difference between duplicates. The relative percent difference (RPD) is calculated by the equation:

$$RPD = \left[\frac{D_1 - D_2}{\frac{1}{2}(D_1 + D_2)} \right] * 100$$

The term "D_1" is the first duplicate sample measurement and "D_2" is the second duplicate sample measurement. The difference between the duplicates is divided by half the sum of the duplicates. The result is multiplied by 100 for RPD. The standard deviation or relative standard deviation can also be used to estimate precision. The relative standard deviation is calculated by dividing the standard deviation by the average concentration.

The MQO for accuracy must specify how much systematic error or bias is acceptable. Accuracy is measured by calculating percent recoveries of analyte organic surrogates, radioanalytical tracers, matrix spikes, and laboratory control samples. The percent recovery or average percent recovery is used to calculate the accuracy. The average percent recovery (APR) is calculated by the equation:

$$APR = (\text{X-bar} +/- t \bullet s_{\text{X-bar}}) * 100$$

The term "X-bar" is the average recovery of replicate measurements. The "t" is the Student's t-value for a specific confidence level and degrees of freedom based on "n" (the number of measurements used to estimate the standard deviation), and "$s_{X\text{-bar}}$" is the standard deviation of replicate measurements divided by the square root of the number of measurements ($s/n^{1/2}$).

Associated with the average systematic error of a method is the uncertainty of the bias estimation. The expanded uncertainty interval "+/- $t \bullet s_{X\text{-bar}}$ " is an estimate of the uncertainty associated with the average percent recovery (X-bar). The uncertainty interval is expanded to a specific confidence level such as 95% and it is centered on the average recovery. As the number of measurements increase, the precision of the estimated average percent recovery improves and the measurement uncertainty interval decreases.

Qualitative MQOs

Qualitative MQOs specify representativeness, completeness, and comparability that must be achieved for a particular project. Representativeness is the degree that data accurately and precisely represents the average concentration and the variability of the study population

contaminant concentration. The representativeness MQO specifies the degree of agreement between the sample measurement statistics and the population parameters. Measurement uncertainty can confound representativeness of the sample data. Cross contamination during sampling and sample collector efficiency also affect representativeness.

Completeness is the proportion of usable data compared to the amount of data that is planned. The MQO for completeness specifies the percent of useable data that must be produced. Using the completeness MQO, data is evaluated based on the quantitative MQOs. Data that is between the detection limit and the quantitation limit must be qualified as an estimate because the precision and accuracy of the measurement are unknown. Flagged data can affect the completeness of the data. Other evaluation criteria of completeness include meeting preservation requirements and hold times, and samples lost (from leakage or breakage) during shipping and handling.

Comparability is the confidence that data from different sources are comparable. This includes different sample collection, preparation and test determination methods, or data sets generated by different laboratories performing the same methods that result in comparable or equivalent data. The MQO for comparability specifies the degree that data collected in other studies are similar and the comparison is based on the quantitative MQOs. Results from different laboratories or different methods are comparable when the comparability MQOs are achieved.

Measurement Uncertainty

As stated earlier, the total variability of the study data is a combination of the inherent variability of the study population and the measurement variability. The sources of total study uncertainty must be identified and evaluated to understand the affects of measurement uncertainty on decision making. This requires breaking down or partitioning the components of total study uncertainty and estimating each component's contribution.

Identification of Components of Total Study Uncertainty

The sources of total study uncertainty can be broken down into the following general components:

- Study population
- Sampling design
- Sample collection
- Sample preparation
- Sample test determination

The following figure (Figure 1) represents the components of study variability.

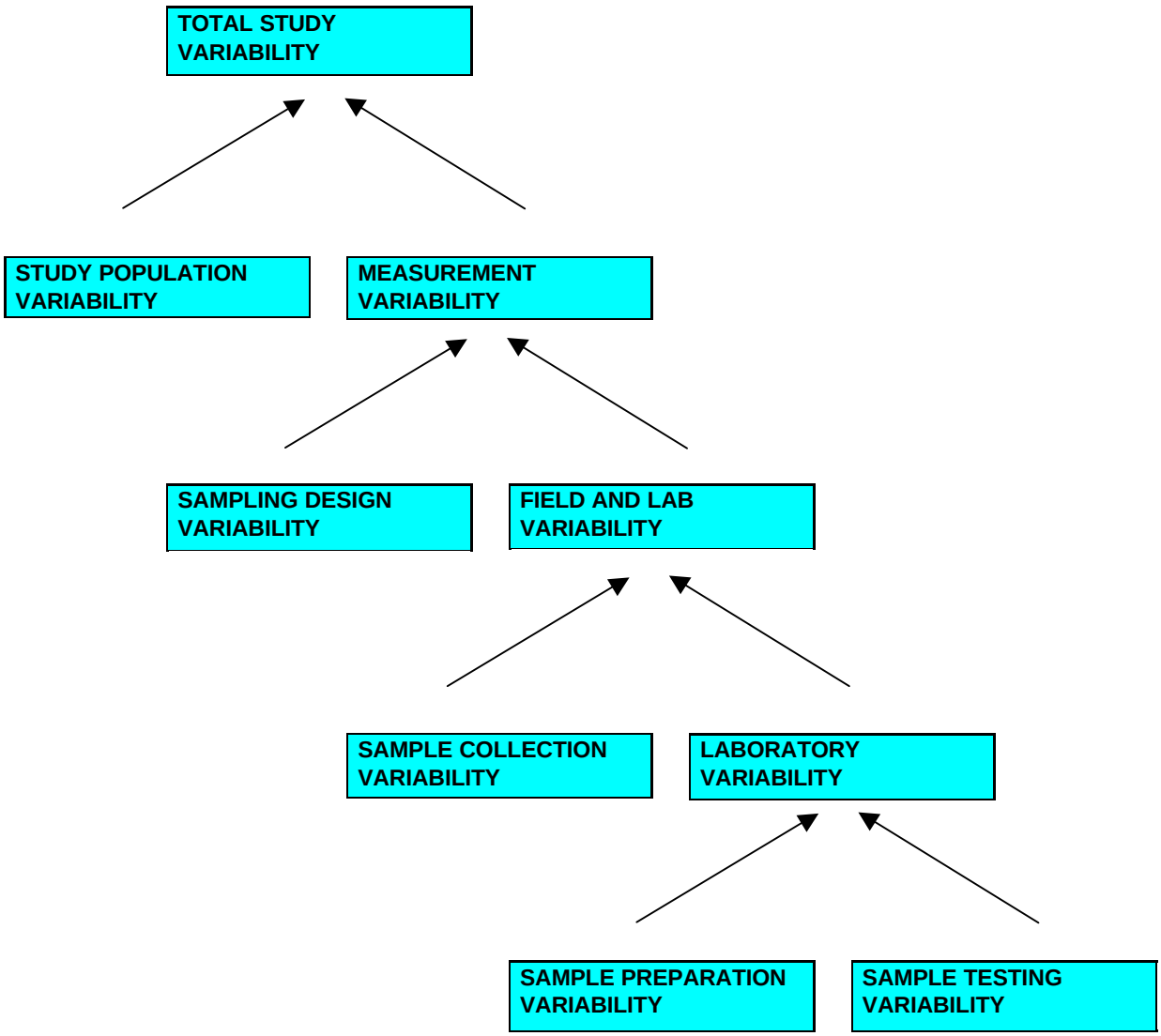

Figure 1. Heirarchy of total study variability components

Component Contribution to Total Study Uncertainty

In Figure 1, the components of total study variability are identified and the functional relationships of the components are flowcharted. Study population variability is the natural variability inherent in the contaminant distribution of the sampling site media. This underlying variability cannot be reduced, but it can be estimated. There may be a wide range in variability of measurement data from a study population that is caused by a complex spatial distribution of the contaminant. Heterogeneous soil and rock media, complex hydrogeologic conditions, contaminant stratification, and geochemical fate and transport processes contribute to the inherent variability of the study population.

Measurement uncertainty is caused by the number and location of samples, sample collection, subsampling, sample preparation, and test determination. This variability affects the confidence in making cleanup decisions for environmental study sites. Decisions to cleanup a site are often based on whether the average contamination concentration of the site is

significantly above background concentrations. The MQOs are used to control the various sources of measurement uncertainties and ensures that data of known quality are generated.

Sampling design uncertainty is affected by the sampling strategy. The sampling frame selection and sampling unit definition as well as the sampling strategy model selected affect the sampling design uncertainty. The number and location of the samples affect the degree of sample representativeness for the study population. As the density of samples increase the sampling design uncertainty decreases. Random, unclustered, and uncorrelated samples increase the accuracy of the estimated average contaminant concentration. When samples are not random, unclustered, and uncorrelated, geostatistical evaluation must be applied to the data.

The sample collection personnel competency, volume or mass collected, and sample collector efficiency affect sample collection uncertainty. During sampling events cross contamination between samples, sample preservation, and analyte degradation also affect sample collection uncertainty.

Physical and chemical preparation processes affect preparation uncertainty. Physical preparation includes sample homogenization, particle size reduction, and subsampling. Chemical preparation includes extraction, separation, and concentration. Each tier of the preparation process affects the percent recovery of the analyte.

Matrix interferences affect both preparation and test determination. Refractory matrices inhibit extraction of the analytes while co-precipitation of interferents inhibits during concentration and separation procedures analyte recovery. Co-elution of interferents (during instrumental determination) affects method selectivity while carryover from high concentration samples affect following samples test determinations. Instrumental fluctuation affects intrinsic measurement repeatability and contributes to irreducible measurement uncertainty.

Evaluation of Components of Total Study Uncertainty

The total study uncertainty used in the DQO process is a combination of study population variability and measurement uncertainty. The following general equation is used to evaluate uncertainty that represents the sources of total study uncertainty. The term "s_r^2" is the relative standard deviation of replicate measurements squared:

$$\underset{\text{(DQO)}}{{}^{\text{Total Study}}s_r^2} = \underset{}{{}^{\text{Inherent Population}}s_r^2} + \underset{\text{(MQO)}}{{}^{\text{Measurement}}s_r^2}$$

The relative standard deviations are squared because the variances are summed in quadrature (square root of the sum of the squares). If the MQO measurement uncertainty (represented by the relative standard deviation, s_r) is less than 1/3 of the inherent population variability, then less than 10% of the total study variance is derived from measurement uncertainty. For example, if the relative standard deviation of the inherent population variability is 30% and the measurement relative standard deviation is 10%, then the total study is 33% relative standard deviation. The following equations represent the calculations for total study relative standard deviation or relative standard uncertainty.

$$^{\text{Total Study}}S_r^2 = 30^2 + 10^2$$

$$^{\text{Total Study}}S_r^2 = 900 + 100$$

$$^{\text{Total Study}}S_r^2 = 1000$$

$$^{\text{Total Study}}S_r = 33$$

Measurement uncertainty can be broken down into uncertainty derived from sampling design, field sample collection, and laboratory preparation and test determination. The following equations are a tiered break down or partitioning of the measurement process.

$$^{\text{Measurement}}S_r^2 = {}^{\text{Sampling Design}}S_r^2 + {}^{\text{Field and Lab}}S_r^2$$

$$^{\text{Field and Lab}}S_r^2 = {}^{\text{Field Sample Collection}}S_r^2 + {}^{\text{Laboratory}}S_r^2$$

$$^{\text{Laboratory}}S_r^2 = {}^{\text{Sample Preparation}}S_r^2 + {}^{\text{Sample Test Determination}}S_r^2$$

The equations are based on the Figure 1 hierarchy of components of total study uncertainty. To estimate the variance from each tier of the hierarchy, the equations are modified by representing the variance results with routine field and quality control samples. The relative standard deviation for each quality control sample is estimated and squared to calculate the variance. After determining the variances for each component, the square root of the variance is taken to determine the relative standard deviation. This is the component relative standard uncertainty. The following equation represents the uncertainty associated with routine field samples:

$$^{\text{Total Study (Routine Field Samples)}}S_r^2 = {}^{\text{Inherent Population}}S_r^2 + {}^{\text{Measurement}}S_r^2$$

Routine field samples are measured to determine the statistics of contaminant average concentration and standard deviation. By estimating the measurement relative standard uncertainty (represented by the relative standard deviation) the inherent population variability (represented as a relative standard deviation) can be estimated. Normally the relative standard uncertainty is expanded to the 95% confidence level. As the underlying heterogeneity of the study population increases, the need for a higher density of samples increases. Stratified sampling that breaks down the study-sampling site into similar discrete sampling areas may also be required.

The measurement variability of quality control samples is used to quantify the uncertainty contribution from different sources or components of measurement uncertainty. This requires partitioning the components of variability that contribute to the measurement variability of the quality control samples. The following equation represents the uncertainty associated with co-located samples:

$$^{\text{Measurement (Co-Located Sample)}}S_r^2 = {}^{\text{Sampling Design}}S_r^2 + {}^{\text{Field and Lab}}S_r^2$$

Co-located samples are collected 0.5 to 3.0 feet from the original field sample to estimate

between sample location variability. Co-located sample measurement variability is a combination of test determination uncertainty, sample preparation uncertainty, matrix interference uncertainty, sample collection uncertainty, and sampling design uncertainty.

Field duplicate samples are collected at the same sample location, but split in the field and sent to the laboratory for testing to estimate sample collection variability. The field duplicate sample measurement variability is a combination of test determination uncertainty, sample preparation uncertainty, matrix interference uncertainty, and sample collection uncertainty. The following equation represents the uncertainty associated with field duplicate samples:

$$\text{Field and Lab (Field Duplicate [Split] Sample)}S_r^2 = \text{Field Sample Collection}S_r^2 + \text{Laboratory}S_r^2$$

Laboratory duplicate matrix spiked samples are field samples that are spiked with the study analyte to estimate sample preparation and test determination variability. Laboratory duplicate matrix spiked sample variability is a combination of test determination uncertainty, sample preparation uncertainty, and matrix interference uncertainty. The following equation represents the uncertainty associated with laboratory duplicate samples:

$$\text{Laboratory (Laboratory Duplicate [Matrix Spiked] Sample)}S_r^2 = \text{Sample Preparation}S_r^2 + \text{Sample Test Determination}S_r^2$$

In addition to the field samples, the laboratory also prepares and tests laboratory control samples, calibration standards, and calibration verification standards. The laboratory control sample is a clean matrix (interference-free) sample spiked with the study contaminant and it is used to evaluate laboratory preparation and testing capabilities. The laboratory control sample measurement variability is a combination of the test determination uncertainty and the sample preparation uncertainty. The sample test determination uncertainty (intrinsic instrumental measurement repeatability) can be estimated by replicate measurement of the same prepared sample. This can include field samples, laboratory control samples, or calibration standards. The only caveats are that the same prepared sample must be repeatedly determined to estimate test determination uncertainty, and test results must be greater than the PQL, but lower than the limit of linearity for the instrument. One alternative is to calculate the sample test determination relative standard deviation from replicate testing of the same prepared field sample with an analyte concentration near the action level. Another alternative is replicate test determinations of the calibration standard to estimate the relative standard deviation of the test determination.

Example MQOs

The MQOs are often established to support the data user's decision of whether the average contaminant concentration is less than a regulatory or action level. Uncertainty in the decision is contingent on the total study uncertainty and reducing total study uncertainty improves the quality of environmental cleanup decisions.

As stated before, total study uncertainty is derived from a combination of inherent population variability and measurement uncertainty. Measurement uncertainty impacts each of the MQOs and controlling measurement uncertainty is a goal of MQO development. Measurement uncertainty is partitioned or divided into the following components.

$$^{Measurement}S_r^2 = {}^{Sampling\ Design}S_r^2 + {}^{Field\ Sample\ Collection}S_r^2 + {}^{Sample\ Preparation}S_r^2 + {}^{Sample\ Test\ Determination}S_r^2$$

Any one of these components can be partitioned or broken down into subcomponents and MQOs can be developed for these subcomponents.

Quantitative MQOs

The quantitative MQOs are detection/quantitation limits, precision and accuracy. For a certain project, the MQO for detection limit may specify that the MDL must be less than or equal to 2 mg/kg and that the MQO for quantitation limit may specify that the PQL requirement must be less than or equal to 10 mg/kg. The MQOs for precision and accuracy specifies the percent recovery and relative percent difference or relative standard deviation for quality control samples. The percent recovery target for the laboratory control sample may be 80 – 120% to determine accuracy of the preparation and testing methods, and percent recovery target for laboratory matrix spiked samples may be 75 – 125% to determine matrix interference biasing effects. The MQO for precision may be broken down into precision requirement for laboratory duplicates, field duplicates, and co-located samples. The following table (Table 1) is an example list of the precision MQOs for duplicate samples.

Table 1. MQOs for Duplicate Samples

Quality Control Sample	Relative Percent Difference
Laboratory Duplicate Matrix Spiked Samples	**+/-20**
Field Duplicate Split Samples	**+/-35**
Co-located Duplicate Samples	**+/-50**

Qualitative MQOs

The qualitative MQOs are representativeness, completeness, and comparability. The MQO for representativeness may specify that the uncertainty of the measurement must be less than 1/3 of the inherent population variability. The MQO for completeness may specify that 90% of the planned data must be usable. The MQO for comparability may specify that the reporting limit for measurement results must be less than 1/10 the action level.

Achieving MQOs

As stated before, MQOs specify “what” the levels of data performance must achieve, but do not specify “how” those levels of data performance will be achieved. To achieve the target MQOs, strategies and methods are selected that together meet the MQO criteria. Because MQOs are the data characteristic that control measurement uncertainty, specifying the acceptable uncertainty for sampling strategies, sample collection methods, and sample preparation and test determination methods is required. The specification of MQOs however must also be realistic and take into account fundamental or irreducible uncertainty associated with each activity. Achieving MQOs must start with planning realistically achievable MQOs. This would include an evaluation of the available sampling and testing methods, and the estimation of measurement uncertainties associated with them.

An identification and evaluation of the sources of measurement uncertainty provides the framework for selecting the appropriate strategies and methods. A simple random sampling

strategy requires fewer samples than a random start systematic grid strategy, but greater bias and uncertainty is associated with simple random sampling than systematic grid sampling. Composite sampling reduces the number of samples prepared and tested by the laboratory, but composite samples may mask underlying “hot-spot” contamination and correlation in the distribution of contaminants.

Identification of “weak links” in the hierarchy of components that contribute to total study uncertainty may indicate that definitive testing methods with narrow uncertainty intervals do not significantly decrease the total study uncertainty because of the underlying heterogeneity of the media. In that case, additional samples coupled with less-definitive methods (such as screening methods) with wider uncertainty intervals may achieve the target MQOs in support of the decision of the data user while remaining within the budgeting, scheduling, and performance constraints. One laboratory may have a lower cost than another laboratory. The lower cost laboratory may have a higher report limit (4.0 mg/kg vs. 0.4 mg/kg) and wider precision limits (+/-20% RPD vs. +/-10% RPD) than the higher cost laboratory. However, the lower cost laboratory may be acceptable because it meets the target MQOs for report limit and precision.

A systematic project planning, design, implementation, and evaluation program is required to achieve MQO targets. Because both sample density and data precision can affect the total study uncertainty, a strategy that balances sampling and testing uncertainties to achieve the MQO targets is the best approach. This approach requires establishing realistic MQOs derived from the project DQOs, identifying and evaluating the contribution to total study uncertainty of each component of the sampling and testing process, selecting the appropriate procedures, and determining whether the target MQOs are achieved.

PERFORMANCE-BASED DATA EVALUATION
The evaluation of environmental chemical data with respect to project-specific objectives

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ABSTRACT
The U.S. Army Corps of Engineers (USACE) is in the process of using a more performance-based approach for evaluating environmental chemical data. The final draft USACE document, "Guidance for Evaluating Performance Based Chemical Data," presents data evaluation strategies that are more dependent upon project-specific objectives and are substantively applicable to any instrumental chemical method. The basic technical approach is summarized and several data qualification strategies are presented for the purposes of illustration.

INTRODUCTION
The production of data of "known and acceptable quality" is a primary goal of every environmental restoration and compliance sampling and analysis activity. Some degree of data evaluation is usually required to ensure that only scientifically defensible data are used to support decisions. However, the extent and nature of the analytical testing and subsequent data assessment activities will be dependent upon the project's data quality objectives (i.e., qualitative and quantitative statements that specify the quality of data required to support the decision making process). This is consistent with the underlying philosophy of a "performance-based measurement system" (PBMS). The USEPA Environmental Monitoring Management Council defines a PBMS as "a set of processes wherein the data quality needs, mandates or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those needs in a cost-effective manner." This implies that the implementation of a PBMS inherently requires data evaluation to be performed with respect to project-specific objectives and will involve some degree of data usability assessment.

Unfortunately, there is no standard for evaluating (i.e., reviewing or validating) chemical data with respect to project-specific data quality objectives (DQOs). For example, the USEPA Contract Laboratory Program (CLP) National Function Guidelines (NFGs) for Inorganic and Organic Data Review, the environmental testing industry's *de facto* standard for validating chemical data, specify fixed contractually-based evaluation criteria that will not be appropriate for all projects and cannot be directly applied to "non-CLP" methods (i.e., methods not listed in the CLP Statement of Work). The data evaluation process defined by the NFGs was not designed for usability assessment and can result in an over estimation of data quality. Even if it were possible to specify a set of fixed quality control (QC) acceptance limits for all data uses (e.g., using the acceptance limits in the NFGs), it would not be practical to propose an evaluation strategy for every combination of QC problems that could be encountered. The

potential for multiple QC problems with respect to different DQOs suggests that a prescriptive approach is not viable. Because of the complexities of environmental investigations and uniqueness of environmental samples, analytical data must ultimately be evaluated using professional judgment in the context of project-specific DQOs.

In order to effectively evaluate analytical data, the evaluator must understand the intended use of the data. To accomplish this, the evaluator should be involved in the early planning stages of the project (e.g., should participate in "scoping" meetings where project DQOs, scheduling, sampling techniques, analytical methodologies and data evaluation criteria are established). Data evaluation should not be performed as a "last-minute" activity that is initiated only after all sample collection and analysis activities have been completed. At a minimum, the evaluator should receive input from the end-data users regarding the objectives of the analyses by reviewing project documents such as the Sampling and Analysis Plan (SAP) and the Quality Assurance Project Plan (QAPP).

The USACE has developed a more performance-based (i.e., "DQO-driven") approach for evaluating analytical data. The document "Guidance for Evaluating Performance-Based Chemical Data Packages," which USACE is currently in the process of publishing as "Engineer Manual 200-1-10," presents guidance for evaluating chemical data that is applicable to essentially any instrumental method. The document defines a "performance-based method" as an analytical procedure for which precision, accuracy, completeness, representativeness, comparability and sensitivity (PARCCS) are demonstrated and documented for the analytes of concern in the media of concern at levels of concern (i.e., at or below the project's action levels). As in conventional approaches for data evaluation, laboratory performance is evaluated using QC samples such as laboratory control samples and method blanks. Matrix effects are evaluated using matrix spike, surrogate spike and post digestion spike recoveries. Field samples such as field blanks and duplicates are used to evaluate QC problems associated with sample collection activities. At a minimum, data packages are evaluated with respect to the following elements:

- Completeness
- Holding times and preservation
- Initial calibrations
- Continuing calibrations verifications
- Initial calibration verifications
- Detection, quantitation and reporting limits
- Blanks (e.g., field and laboratory method blanks)
- Spike Recoveries (e.g., for laboratory control samples, surrogates and matrix spikes)
- Duplicates (e.g., matrix spike/matrix spike duplicates)

However, unlike conventional approaches, the USACE document presents data evaluation strategies rather than prescriptive QC acceptance limits. In addition, data is evaluated with respect to method quality indicators (i.e., PARCCS) as a *first-step* process for data usability assessment. In conventional approaches, analytical data are usually evaluated (e.g., qualified) with respected to pre-determined QC acceptance limits and little or no usability assessment is performed. For example when validation is performed using the NFGs, sensitivity is evaluated with respect to fixed Contract Required Quantitation Limits (CRQLs)

rather than project-specific action levels. However, meeting CLP CRQLs does not necessarily ensure that the data will be usable (a problem which, unfortunately, many usability assessments also fail to identify). The USACE document constitutes a more streamlined approach. During "performance-based data evaluation," data quality is evaluated (at least to some degree) with respect to the end use of the data.

It should be noted that, although the data evaluation strategies in the USACE guidance can result in a relatively thorough evaluation of data quality, they might not be adequate for all data uses. The USACE guidance primarily addresses the evaluation of only instrument calibration and batch QC samples (e.g., method blanks and laboratory control samples). Reported results are not evaluated to the level of the raw data (e.g., chromatograms and other instrumental printouts). Instrument QC samples (other than for calibration) are assumed to be in control or out-of-control in a manner that is consistent with the performance of the batch QC samples. This assumption is usually reasonable but is not always valid. During project planning, factors such as the objectives of the analyses, the nature of the contamination, the limitations of the analytical methodology and information about past waste handling activities at the site must be taken into account to determine the level of effort required for the data evaluation. For example, when pesticides are being analyzed by Method 8018A, it may be necessarily to evaluate the Endrin breakdown check as well as batch QC results (e.g., the laboratory control sample and matrix spike recoveries), to determine whether or not detections of Endrin ketone and Endrin aldehyde are false positives arising from the degradation of Endrin during instrumental analysis. However, based upon the historic information and the "risk divers" for a particular study area, a comprehensive evaluation of low-level detections of Endrin degradation products may not be required and the evaluation of batch QC sample (e.g., laboratory control samples and matrix spike recoveries) may be completely adequate.

PERFORMANCE-BASED DATA EVALUATION - Some salient elements that differ from conventional approaches

Data qualification is an integral component of data review and validation and primarily results in a *qualitative* evaluation of analytical data; that is, measurement uncertainty is not quantified (which is another reason why data review and validation do not usually result in a full assessment of data usability). Data qualifiers or "flags" are primarily applied to sample results when pre-determined QC acceptance limits are not met. During performance-based data evaluation, data qualifiers are also applied to identify quality problems that may impact the usability of the data. However, unlike conventional approaches, performance-based data evaluation is highly dependent upon the reviewer's understanding of the objectives of the project. In particular, when a QC problem is observed (e.g., a QC acceptance limit is not met) and project-specific action levels are available, data are qualified on the basis of the direction of bias, the (estimated) magnitude of the uncertainty associated with the QC failure and the proximity of the contaminant concentrations to the action levels (i.e., the levels at which the analytes of concern are being monitored).

Furthermore, when conventional data validation is performed (e.g., using the NFGs), data are typically qualified as either *estimated* (e.g., with the *J flag*) or *rejected* (e.g., with the *R flag*). However, results are frequently rejected only for the most severe or blatant QC problems; in practice, the *R flag* is rarely applied. When QC problems are observed, the data are qualified as *estimated* and are subsequently used to support project decisions. Unfortunately, *J*-flagged

data are sometimes used to support project decisions without evaluating the impact of the QC problems on the usability of the data, resulting in an over estimation of data quality. To exacerbate matters, analytical service providers (e.g., to avoid financial penalties) and their clients (e.g., to facilitate the approval of the data by regulators) often adopt inappropriately wide QC limits to avoid reporting too much *J*-flagged (or *R*-flagged) data.

During performance-based data evaluation (as defined by the USACE guidance), data associated with QC problems are primarily qualified as *estimated* (*J flag*), *tentatively rejected* (*X flag*), or *rejected* (*R flag*). Data associated with a marginal QC failure that are believed to be tentatively usable or "more usable than not" are qualified as *estimated* (i.e., estimated and tentatively usable). Data associated with a gross QC failure are qualified as rejected. Data that are "mostly unusable" or that fall into the "gray area" between *estimated* and *rejected* are qualified as *tentatively rejected* (i.e., estimated and tentatively rejected). The distinction between *estimated*, *tentatively rejected* and *rejected* data resides in the degree of the QC failure and is dependent upon the reviewer's understanding of the objectives of the project. The use of the *X* flag minimizes the potential indiscriminate use of *J*-flagged data. Tentatively rejected data would not be used to support project decisions unless the data user were to present (i.e., document) some technical rationale for doing so (i.e., the data would ultimately be rejected in the absence of a scientifically defensible rationale to do otherwise).

Two examples are presented to illustrate how data evaluation can be performed using a more performance-based approach. Some conventional data qualification protocols are compared with data qualification strategies from the USACE guidance. The first example addresses the evaluation of measurement quality objectives for sensitivity and the second example addresses the evaluation of measurement quality objectives for accuracy.

EVALUATION OF SENSITIVITY

According to the NFGs for Organic Data Review, an objective of the data evaluation for the CLP VOA analyses is to "ensure that the reported quantitation results and Contract Required Quantitation Limits (CRQLs) are accurate" (USEPA, 1994, p. 39). The evaluation of CRQLs primarily involves verifying "CRQLs have been adjusted to reflect all sample dilutions and dry weight factors that are not accounted for by the method." For the low-concentration water method, the CRQLs for the "non-ketones" are one part-per-billion (ppb), the concentration of the lowest initial calibration standard (USEPA, 1994, p. 12 - 13). Detections less than the CRQLs are reported as estimated using the J qualifier and nondetections are reported using the U qualifier (i.e., are reported as "1 U").

Consider a project where groundwater is being analyzed by the low-level CLP VOA method to determine whether or not vinyl chloride is present at concentrations less than 0.1 ppb. However, assume that the laboratory's method detection limit (as determined by 40 CFR, Part 136, Appendix B) is 0.4 ppb. If a result of "1 U" is reported for a groundwater sample, the result is validated using the criteria described in the NFGs, and no problems are identified with respect to these criteria (e.g., the CLP CRQL is verified), then the result would not be qualified as either estimated or rejected. However, a result of "1 U" obviously does not demonstrate that vinyl chloride contamination is above or below the 0.1 ppb action level. The result is unusable for monitoring contamination at 0.1 ppb because analytical sensitivity is

inadequate. According to the data qualifications protocols in the USACE guidance document, the result would be reported as “1 X” or “1 UX”. For example, Section 6 of the guidance (“Sensitivity: Detection, Quantitation and Reporting Limits”) states: “If an action level (AL) is available, compare the MRL [method reporting limit] to the AL. *If the MRL is greater than the AL, qualify nondetections with the X or XU flag (since false negatives have not been adequately addressed).*”

Let us increase the action level by a factor of ten (i.e., assume that contamination is being monitored with respect to an action level of 1 ppb) and assume that a detection of “0.8 J” is reported for vinyl chloride. If the method detection limit is 0.4 ppb, does a detection of “0.8 J” indicate that vinyl chloride is present in the groundwater at a concentration less than 1 ppb? Since the action level is near the detection limit and detection limits can vary by a factor of two in a clean matrix, the analytical uncertainty is relatively high. It is reasonable to assume that the error near the action level is at least ± 0.4 ppb. When the magnitude of the analytical error and the proximity of the detection to the action level are taken into account, the result is potentially unusable for determining whether or not contamination is less than 1 ppb (e.g., assuming that the result is not part of a set of replicate measurements being used to test a statistical hypothesis).

It should also be noted that the CLP requirement to set the lowest initial calibration standard at 1 ppb is typically insufficient to ensure reliable quantitation at this level. An evaluation of the quantitation limit should also involve an examination of the “goodness-of-fit” of the initial calibration line near the action level as well as an evaluation of the detection limit (e.g., the detection limit should typically be much less than the quantitation limit). In this example, sensitivity requirements were not adequately evaluated during project planning. The quantitation limit was established using the lowest initial calibration standard, but should have been well below the 1-ppb action level and well above the detection limit (e.g., at least five to ten times greater than the detection limit). Furthermore, it would have been desirable to evaluate the accuracy of the laboratory method by spiking laboratory control samples near (e.g., within a factor of two) the 1-ppb action level.

During performance-based data evaluation, if laboratory control samples spiked at or near the action level were not processed (e.g., to evaluate the magnitude of the uncertainty at this level), the quantitation limit for vinyl chloride would be estimated to be five to ten times the method detection limit (i.e., about 2 to 4 ppb). For example, Section 6 of USACE document states:

If the lowest calibration standard is not at least five times greater than the MDL and an acceptable low-level CCV or LCS was not analyzed to verify the MQL then the initial calibration results must be evaluated… If it is not possible or practical to determine the MQL from the calibration data, then set the MQL to five to ten times the MDL, but indicate that the MQL is an estimate in the data evaluation report.

Since the action level is less than the estimated quantitation limit, detections less than the action level would be qualified as tentatively rejected (i.e., potentially unusable). For example, the vinyl chloride detection would be reported as “0.8 X” rather than “0.8 J.”

EVALUATION OF ACCURACY

Assume that accuracy is being evaluated using surrogate recoveries using the data qualification protocols in the NFG for Organic Data Review. In particular, according to the NFGs for Organic Data Review, the aqueous acceptance ranges for the surrogates phenol-d5 and 2,4-6-tribromophenol are 10% - 110% and 10% - 123%, respectively (USEPA, 1994, p. 66 - 68). Therefore, surrogate recoveries greater than 10% (e.g., for method blanks and environmental samples) would not trigger any data qualification. These acceptance ranges may be indicative of typical laboratory performance but may not satisfy project data quality objectives for accuracy. Recoveries as high as 20% or 30% are still indicative of severe low analytical bias. The data qualification with respect to these wide contractual limits will potentially result in an over estimation of the quality and usability of the data.

For the purpose of illustration, assume that 2,4,6-trichlorophenol is being monitored in groundwater with respect to an action level of 20 ppb and detections of 2,4,6-trichlorophenol ranging from 10 to 15 ppb are associated with surrogate recoveries falling within 10% - 120%. In general, the detections do not demonstrate that 2,4,6-trichlorophenol is present in the groundwater at concentrations less than the 20-ppb action level. If the laboratory's statistical control limits for surrogates in laboratory control samples are approximately 65% ± 55% (i.e., 10% to 120%), with some simple assumptions, the laboratory's in-house control limits can be used to estimate an upper bound (with respect to laboratory measurement uncertainty) for the detected concentrations of 2,4,6-trichlorophenol (T. Georgian, 2000). If it is assumed that the surrogates behave in a similar manner as 2,4,6-trichlorophenol and the recoveries are normally distributed, then the mean surrogate recovery (65%) can be used to correct the measured concentrations for bias for the purpose of data qualification. (Because of random error, the mean surrogate recovery is a better measure of analytical bias than any single surrogate recovery.) The following equation in Section 11 of the USACE guidance can be used to estimate a 99% confidence interval for 2,4,6-trichlorophenol:

$$100\ \ (c\,/\langle R\rangle)\ \ (1\ \pm\ L\,/\,\langle R\rangle)$$

The variables $\langle R\rangle$, c and L represent the mean surrogate recovery (e.g., 65%), the detected (i.e., measured) concentration of 2,4,6-trichlorophenol (e.g., 10 ppb) and the half width of the surrogate recovery control range (e.g., 55%), respectively. Therefore, for a measured concentration of 10 ppb, the confidence interval is approximately

$$15 \text{ ppb } \pm \text{ 13 ppb}$$

With respect to only laboratory analytical uncertainty, a measured concentration of 10 ppb represents an actual sample concentration as high as 28 ppb, and does not demonstrate that the analyte concentration is less than the 20-ppb action level. The detection of 10 ppb should be qualified as potentially unusable (e.g., with the "X flag"); at a minimum, the result should be reported as estimated with low bias (e.g., using the "J- flag").

It should be noted that a single surrogate recovery could be used to estimate a 99% confidence interval:

$$100\ \ (c\,/\,R)\ \ (1\ \pm\ \sqrt{2}\,L\,/\,R\,)$$

The variable *R* denotes a single recovery (rather than a mean recovery) associated with a measured result *c*. For example, if 2,4,6-trichlorophenol were detected at 10 ppb in a groundwater sample and the recovery for the surrogate 2,4-6-tribromophenol was 30% (i.e., R = 30%), then the following confidence interval would be obtained:

33 ppb ± 86 ppb

This would result in a more conservative estimate of the upper bound concentration but the lower bound of the confidence interval would not be physically meaningful because of the large uncertainty associated with the bias correction (e.g., a single recovery of 30% is not statistically different from zero given that recoveries vary within ± 55% due to random error).

The discrepancy between the data qualification protocols in the NFGs and the USACE performance-based data evaluation guidance resides in the selection of the QC acceptance limits and the use of project-specific decision limits to evaluate data quality. In the NFGs, data qualification is performed with respect to "one-size-fits-all" acceptance limits (e.g., 10% to 120% for the acid faction surrogates) and the magnitude of the uncertainty associated with the acceptance limits or QC failures relative to project-specific action levels is not taken into account. This may be useful for evaluating contractual performance, but, in general, is not of value for evaluating data usability; the evaluation essentially results in contract performance monitoring. The selection of wide acceptance limits (e.g., because of inherent method performance limitations) does not address data usability; the tolerance for measurement uncertainty must be small relative to proximity of the results to the project action limits. Data qualification should address the magnitude of the measurement uncertainty relative to the levels of concern. For example, an acceptance range of 80 – 120% for surrogate recoveries may be adequate to demonstrate that detections ranging from 10 to 15 ppb are less than a 20-ppb action level but an acceptance range of 10% - 120% would be inappropriate.

SUMMARY

The data evaluator should possess a comprehensive understanding of the intended use of analytical data prior to performing any evaluation activities. The evaluator should receive input from the data users regarding the objectives of the project by actively participating in the project planning process and should be aware of the QC requirements in project documents such as the QAPP. Analytical data should subsequently be evaluated with respect to project-specific criteria (e.g., the action levels that trigger cleanup or other remedial efforts) rather than contractual specifications or method-required acceptance limits. Data evaluation with respect to fixed contractual specifications that fails to address analytical error in a holistic manner is of little or no value for assessing data usability. The USACE final guidance draft proposes a more performance-based approach; data are evaluated with respect to project-specific objectives to a greater extent relative to conventional approaches for data validation or review.

ACKNOWLEDGEMENTS

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THE JOY (AND PAIN) OF OVER THE SHOULDER DATA

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The ability to receive effective data on a near real time basis is completely changing operations in the field. Project Managers are quickly realizing the benefit of receiving more and better focused data to help direct their efforts.

Field analysis allows field teams to make effective decisions about a site pretty much real time. This means they can more effectively direct efforts, confirm or disprove anomalies and collect samples that tell them something about the site instead of chasing 'not detects'.

Of course, the saying "be careful what you ask for…" applies here. Project Managers have to deal effectively with the potential deluge of information and the surprises that are inevitable. By the way, they still have to do all of that other stuff they were doing before.

This presentation will discuss the benefits and challenges of 'over the shoulder' results, give some examples and look at some of the things we need to do as field analysis continues to become the standard practice.

RAPID DETECTION OF VOCS USING DIRECT PUSH SAMPLING WITH DIRECT SAMPLING ION TRAP MASS SPECTROMETRY

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Direct push sampling coupled with real-time analytical tools have been developed to reduce the time and cost required for site characterization. Direct-push sensors are available capable of detecting specific classes of contaminants such as petroleum hydrocarbons, explosive compounds, radionuclides, metals, semi-volatile organic compounds and volatile organic compounds (VOCs). This paper describes the demonstration of a direct-push sensor that can quantify VOC contamination in the subsurface in real-time. This system consists of a Membrane Interface Probe (MIP) manufactured by Geoprobe Systems coupled to a direct sampling ion-trap mass spectrometer (ITMS). The ITMS-MIP system was shown to rapidly collect and analyze samples from the subsurface, regardless of matrix. Two of the five demonstrations discussed resulted in a strong linear correlation (r^2 = 0.9) with validation samples analyzed using EPA Method 8260, while the other three demonstrations revealed that the calibration method used in this work introduced a bias compared to EPA Methods.

RAPID ADAPTIVE SITE CHARACTERIZATION: FOLLOWING THE PLUME

S. Pitkin

No abstract available.

PRACTICAL APPLICATIONS OF PBMS

C. Schultz and J. Adelson

No abstract available.

ASTM PBMS EFFORTS

L. Williams

No abstract available.

MISLEADING ASPECTS OF CURRENT COMMONLY USED QC PRACTICES - OR CRAZY THINGS WE DO EVERY DAY

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Due to the competing demands of many stakeholders environmental testing has developed several routinely used procedures that are less than optimal or even counter-productive. Justification is claimed from interpretation of language in EPA methods that may be counter to the original intent of the authors. This paper will describe examples selected from:

- Setting detection limits
  - Pros and cons of instrument specific detection limits
  - Weaknesses of the MDL procedure
  - Alternatives
- Calibration
  - Weaknesses of current protocols
  - Problems with the correlation coefficient
  - Alternatives
- Matrix spikes
  - Application of matrix spike results to unrelated samples
  - Alternatives
- Surrogate spikes
  - The ultimate measure of method performance
  - Possible improvements to current use of surrogates

The reasons for the current state of affairs will be discussed, along with possible alternative techniques and QC protocols.

Poster Papers

COMPARISON OF SW-846 AND CLP ORGANIC METHODS WITHIN THE LABORATORY ENVIRONMENT

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ABSTRACT

This paper discusses the similarities and differences between the Solid Waste (SW-846) and Contract Laboratory Program Statement of Work (CLP SOW) organic analytical methods, within the laboratory environment. While both procedures utilize the same instrumentation and general scientific approach, there are significant differences in the way samples are managed, analyzed, and reported. The CLP is designed to be rigid and withstand legal challenge while the SW-846 methods are written to be flexible and applicable across a broad range of industries. This paper highlights the purposes and objectives of the two programs and examines the benefits and restrictions of each method, from the laboratory's perspective. We will also compare the regulatory approach, discuss the analytical and QC requirements, and examine the deliverables for each. This paper will allow data users to select the approach that best fits their analytical goals through a better understanding of the respective methods.

INTRODUCTION

We would like to outline these analytical methods within their respective programs, compare the approach for each, discuss the QC requirements and examine the deliverables. While doing this, we will present the similarities and differences of each program along with some benefits that each method offers. We hope this discussion will allow the reader to employ the approach that best fits their analytical goals.

BACKGROUND

The Environmental Protection Agency (EPA) Office of Solid Waste has compiled a series of analytical methods (SW-846) which provide sampling and testing procedures as related to the Resource Conservation and Recovery Act (RCRA) program. The methods include instrumentation requirements, analytical procedures, quality control, pertinent compound lists and approximate method detection limits. The aim of these methods is to determine if a waste is hazardous and assist in the subsequent disposal or management of the evaluated material.

The Contract Laboratory Program (CLP) is designed to provide the EPA with analytical data to support the Superfund Program (CERCLA and SARA). This support is through a network of environmental laboratories which receive and analyze samples from the EPA on a contractual basis. Included in this arrangement is a Statement of Work (SOW) which specifies the instrumentation, analytical methodology, target compound list, QA/QC criteria and reporting requirements for each Sample Delivery Group (SDG). This system gives EPA information regarding public health concerns, site cleanup evaluation and liability assessments.

The CLP program provides direction for volatiles and semi-volatile analyses by GC/MS, and

pesticide/Aroclor analysis by GC-ECD. SW-846 has equivalent methodologies for VOAs SVOAs, and pesticides/Aroclors plus numerous other methods encompassing a broad range of instrumentation, matrices and target compounds. We will focus our discussion primarily on the common GC/MS methods, and incorporate other types of analyses where applicable.

TARGET COMPOUNDS

The CLP SOW requires all samples to be analyzed for specific compounds. These compound lists include hazardous substances most often found at Superfund sites and those known to be hazardous to human health. The EPA determines this list and makes minor changes and updates when a new SOW is released. Typically, the contract laboratories are required to analyze and report the full compound list for all Superfund samples. The current SOW (OLM04.2) does include a flexibility clause where minor changes such as adding additional compounds or adjusting the contract required quantitation limits (CRQL) for target analytes may be requested by the user. These modifications must be approved by several parties within EPA (Regional CLP Project Officer or Requestor, CLP Program Manager and the Contracting Officer).

The SW-846 target compound lists are composed of substances which determine whether a particular waste should be considered hazardous. By necessity, this encompasses a broad list of compounds found throughout many industrial processes. The SW-846 methods attempt to provide analytical testing guidance for any compounds which are generated and regulated under the RCRA program.

ANALYTICAL REQUIREMENTS

The following table summarizes various parameters for SW-846 and CLP GC/MS volatile and semi-volatile methods.

Parameter	SW-846 (12/96)	CLP (OLM04.2)
Sample size	1L/30g (SVOA) 5/25ml/5g (VOA)	1L/30g/1g (SVOA) 5ml/5g/1g (VOA)
Matrices	Water/Soil/Oil/Wastes Air sampling media	Water/Soil
Analysis Levels	Low/Med/Direct Injection	Low/Med
Holding times (extraction/analysis)	7/14/40 days (SVOA) 7/14 days (VOA) (Starts at sampling)	5/10/40 days (SVOA) 10 days (VOA) (Starts upon receipt)
Extraction	Acid/Base-Neutral	Acid only
Calibration	5 pt. min./RF/Linear/Quad	5 point/RF
Quantitation	Uses initial calibration	Uses daily calibration/RF's
Batch QC	MS/MSD/LCS	MS/MSD
Method QA/QC	MDL/IDC/PE	PE
Blanks	Method	Method/Instrument/Storage
Target compound list	Open	Fixed
Library search	None	30 largest peaks (TICs)
Quantitation limit	Method determined (MDL)	Fixed (CRQL)
Data Review	In house	EPA review (typically via contractors)

Data Users	Engineering firms, state and local regulatory agencies	EPA Regions
Price	Negotiable	Fixed by contract

QA/QC REQUIREMENTS

Quality control is an important aspect of an environmental laboratory's analytical methods. It is the primary monitoring tool used throughout the procedure to ensure the analyses are functioning properly. The QC procedures are vital during the analysis to determine whether the system is in control and acceptable data is being collected. These same QC parameters are also recorded and monitored over time to plot tendencies and establish baselines for general method performance. The CLP program and SW-846 offer similarities in their QC requirements but also differ in their treatment of outliers and in the long term establishment of trends.

The CLP SOW details the requirements and establishes the limits that each specific batch QC parameter must meet. These include holding time, GC/MS tuning, calibration, surrogate/system compound monitoring recovery, internal standard performance and MS/MSD precision and accuracy. These method limits were developed by examination of CLP laboratory data over the past 20 years. In the laboratory, "CLP limits" are known as those published in the current SOW. Often the laboratory will set up their method to compare the daily or batch QC to these limits, and run samples while the instrument is functioning within this acceptable range. While some QC parameters must be met, such as holding time and tuning parameters, the SOW gives specific instructions on handling other QC parameters that fall outside the SOW QC boundaries. The treatment of outliers in surrogate, internal standard, MS/MSD performance and even some calibration deficiency is addressed so the laboratory can continue to run their analyses. The SOW requires the laboratory to take specific, but finite, action when faced with QC outliers. Typically, surrogate failure is remedied by a calculation check, followed by a rerun and/or re-extraction. After these efforts, the laboratory can report the data and provide discussion via the case narrative. Similarly, internal standard performance failure is followed by sample and internal standard preparation check, demonstration of instrument control and then a rerun and the reporting of either both failures or the one successful run. Although MS/MSD failures are usually reported as is, repeated MS/MSD failure will result in questioning by the Agency. Finally, the CLP methods allow for some compounds to fail calibration criteria (2 VOA/4 SVOA) provided the failures meet certain extended criteria. This availability of clear instructions for handling laboratory data QC outliers enables the laboratory to run samples with confidence, knowing they are within the guidelines of the method and the SOW.

The SW-846 methods, by design, empower the laboratory with the responsibility of designing, implementing and maintaining their QA/QC program. The SW-846 provides guidance through general organic Method 8000 and the respective analytical methods. These methods give a detailed outline of organic laboratory quality assurance goals, procedures, calculations and definitions. The laboratory is encouraged to compile and monitor its QC data over the period of the method application. From this database, control charts, recovery limits and confidence intervals may be determined for surrogates, MS/MSD and laboratory control samples (LCS). This approach is advantageous because the limits generated for a specific instrument include

the various nuances that are unique to each analytical system. SW-846 also gives the laboratory the task of determining the method detection limit (MDL) annually.

Through the policy of allowing the laboratory to implement its own QC system, the SW-846 methods become very adaptable to a variety of compound lists, concentration levels, sample matrices and reporting formats. This approach allows the laboratory latitude in designing its methods to meet a variety of customer needs.

DELIVERABLES

The results of the analyses are reported to the data user in a variety of ways. Some clients are interested in the final numbers while others may require a comprehensive legal document. The requirements of the final report may be the biggest dissimilarity between these two methodologies.

The SW-846 methods, following their wide angle approach, do not give specific instruction for reporting results. The report format is usually designed by the laboratory and agreed upon in advance with the client. Most commercial laboratories offer different levels of reporting, from analytical results, to data plus batch QC results, up to fully validated data packages. More clients are asking for results in electronic format also. Often, a regulatory agency or an intermediate consulting firm determines the reporting requirements.

The Contract Lab Program, conversely, has stringent reporting requirements. The “CLP package” has become the standard in data deliverables. The use of the CLP data package as a model for reporting laboratory results has gained widespread acceptance due to its ability to capture and organize the analytical process from field sampling to storage and disposal.

A large part of the Superfund program deals with potentially responsible party issues. The program seeks to recover the cleanup costs through legal action, which often leads to litigation in the courts. The deliverables are intended to provide documentation in all areas of sample custody, analysis and reporting. This adherence to a consistent and specific format has made the CLP data package the model in laboratory result reporting.

SUMMARY

The availability of the CLP and SW-846 methods provides the environmental laboratory community with two well-developed programs defining the field of environmental laboratory analysis. While both approaches are based on similar scientific technology, their differences allow the laboratory to take advantage of the strength of each method and tailor their services accordingly. The CLP SOW is very strict and gives clear-cut instructions for analyzing samples and reporting them in a standardized format. Most of the decision making is taken off the laboratory which can then concentrate on running samples. The SW-846 methods, in contrast, are meant to be open and flexible in their applications. This allows the laboratory the freedom to design its own quality and reporting systems. This adaptive approach enables the laboratory to meet a variety of client needs and applications.

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ANALYSIS OF WATER FOR PPB RANGE CHLORINATED ORGANICS USING A TOTAL ORGANIC CHLORINE ANALYZER

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ABSTRACT

Dexsil Corporation has recently developed a total halogen method for the analysis of water samples for chlorinated organics. The new procedure is an addition to the existing methods for the L2000DX Chloride Analyzer. The L2000DX has been in use in the field for 12 years and can be used for the analysis of transformer oil, surface wipes and soils. The soil method is the basis for SW-846 Method 9078 "Screening Test Method for Polychlorinated Biphenyls in Soil." Using the same reaction and quantification steps as the established L2000DX methods, the new method uses a liquid-liquid extraction step to achieve method detection limits (MDLs) in the 15-30 ppb range for most chlorinated solvents. This new method will allow nearly real time data to be collected from ground water monitoring wells at a fraction of the cost of laboratory analysis.

This paper describes the new method, the development work in establishing the feasibility of the method and the comparison with SW-846 laboratory methods for spiked samples. Recovery MDLs have been determined for the following analytes: Carbon Tetrachloride, 1,2-Dichloroethane (DCEA), *cis*-1,2-Dichloroethylene (DCEE), *trans*-1,2-Dichloroethylene (DCEE), 1,2-Dichloroethylene (*cis*/*trans* mix), Methylene Chloride, Pentachlorophenol (PCP), Tetrachloroethylene (PCE), 1,1,1-Trichloroethane (TCEA), Trichloroethylene (TCEE) and Vinyl Chloride. As expected, the extraction recoveries vary inversely with the solubility of the analyte in water which, in turn, affects the MDL for the analyte. The MDLs for these analytes range from 16 ppb for carbon tetrachloride to 157 ppb for methylene chloride with the majority around 25 ppb.

The method development data indicate that the L2000DX water method should be an useful tool for monitoring ground water in areas contaminated with chlorinated solvents. Now, one instrument can be used to track contamination in both soil and water. This type of screening can be used for checking the progress of a treatment process, defining the limits of a contamination plume, as well as, monitoring ground water over long periods of time. All of these applications do not require expensive laboratory analysis and the L2000DX can provide the information in the field in 10 minutes.

INTRODUCTION

The L2000DX is a screening tool for chlorinated organic compounds and has been used in the field for the analysis of transformer oil for PCB contamination since 1989. Shortly after its introduction, a method was developed to use the L2000DX for the screening of soils for PCBs. This method eventually became SW-846 Method 9078[1] and has been evaluated in two different forms: first, through the SITE program and, most recently, under the ETV program[2] both run by the USEPA. The procedure for PCBs in transformer oil has just recently been validated through the ETV program and a method has also been developed for use on wipe

samples.[3]

In the late 90s, with the rise of chlorinated solvents and pesticides as contaminants in the environment, the demand grew for the development of L2000DX based methods for other chlorinated compounds in soil. Laboratory experiments and field trials have since demonstrated that the L2000DX, following suitable matrix preparation, is suited to the analysis of basically any extractable chlorinated organic in soil.[4]

As chlorinated solvents leach into ground water and interest in cleaning up old dry cleaning and manufacturing sites grows, so has the need for an L2000DX method for water analysis. The objective of this work was to develop and document a water extraction technique for concentrating organo-chlorine contaminants into an organic solvent suitable for introduction into the L2000DX system.

The L2000DX is a total chlorine analyzer. A requirement for the system is that all chlorine must be chemically converted to inorganic chloride for quantification. By changing the sample preparation steps either total chlorine or total organic chlorine will be measured. There are three elements to the analysis: sample preparation/extraction, converting the organic chlorine present into inorganic chloride using metallic sodium and the quantification of the resulting chloride using a chloride ion selective electrode (ISE). Over the 12 years of its use in the field, the L2000DX has proven to be a very reliable instrument and the ISE based system has been shown to be accurate and relatively free of interferences. (NOTE: All organic chlorine is quantified as the target analyte; however, this is the nature of a TOC measurement and is not an interference, *per se*. Inorganic chloride can be an interference, but can be removed in the matrix cleanup step and, therefore, would not interfere.)

There are four basic corrections necessary to convert the final chloride reading into the equivalent analyte concentration in the desired units. Three of the corrections are derived corrections calculated from the known chlorine composition of the analyte (percent chlorine), the dilution/extraction volumes of the matrix preparation steps and the conversion to the appropriate units. The fourth correction necessary to obtain an useful result is derived from empirical data on the overall efficiency of the analytical steps, including the extraction efficiency from the original matrix, the reaction efficiency for the conversion to chloride, the recovery of the chloride ions in the final buffer solution, etc. The theoretical conversion factors can be calculated for all analytes and tabulated for each matrix, but the correction for recoveries must be experimentally determined for each matrix and each analyte.

After some experimentation, it was determined that a simple liquid/liquid extraction would be the simplest and also effective. Of the commonly used solvents, e.g., hexane, heptane, cyclohexane, it was determined that 2,2,4-trimethylpentane (isooctane) worked well and had the advantage of being less volatile. A liquid/liquid extraction will accomplish two things: by choosing the appropriate solvent, it eliminates interferences due to inorganic chloride and by choosing the correct solvent to sample ratio, a concentration of 1:100 can easily be accomplished.

The effectiveness of a liquid/liquid extraction is determined primarily by the extracted compound and is, therefore, not constant over all possible contaminants. In general,

compounds with a high water solubility will tend to have low recoveries in the solvent layer. Extraction efficiency can also be affected by water quality parameters, e.g., pH, salinity, ionic strength, etc. In this work we set out to determine the extraction efficiency for a liquid/liquid extraction combined with the L2000DX sample preparation as well as the MDL for the quantification of environmentally significant organo-chlorine contaminants.

EXPERIMENTAL

All samples were prepared in 965 mL of deionized water, cooled overnight, in 1-quart glass jars from Quality Environmental Containers. The majority of the water samples were between 11 and 14 ºC when extracted, determined after the extraction was complete. The temperature was varied between 2 ºC and 45 ºC for water samples used to determine the effects of temperature on the extraction of methylene chloride. To study the effects of ionic strength, pH and salinity on the recovery of methylene chloride, deionized water was first spiked with either 1% sodium sulfate, hydrochloric acid (pH < 2), sodium hydroxide (pH>12) or 1% sodium chloride, shaken and then refrigerated. Recovery experiments using PCP were also conducted on pH adjusted water.

Each day, a fresh stock solution of approximately 2500 ppm of a single analyte was prepared in methanol. Appropriate volumes of stock solution were injected by syringe into the cooled water to yield the desired analyte concentrations. Each jar was gently turned to ensure mixing of the analyte, while minimizing its partitioning into the headspace. To determine the method recoveries and linearity, duplicate samples were prepared at the following concentrations: 0.15, 0.25, 0.50, 1.0, 2.0, 5.0 and 10.0 ppm. Additionally, the MDL was determined for each analyte according to 40 CFR Part 136.[5] The seven replicate water samples for each analyte were prepared in the same way at concentrations within a factor of 3-5 of the estimated MDL (See Table 1).

Table 1. Comparison of Recoveries and Regression Coefficients for GC and L2000DX Response Curves

Analyte	L2000DX R^2	L2000DX Recovery	GC/GCMS R^2	GC Recovery
Carbon Tetrachloride	0.974	0.58	xx	xx
1,2-Dichloroethane (DCEA)	0.992	0.18	0.991	0.95
cis-1,2-Dichloroethylene (DCEE)	0.987	0.26	xx	xx
trans-1,2-Dichloroethylene (DCEE)	0.987	0.41	xx	xx
1,2-Dichloroethylene (*cis*/*trans* mix)	0.99	0.26	0.99	1.15
Methylene Chloride	0.992	0.09	xx	xx
Pentachlorophenol (PCP)	0.996	0.54 (0.6@pH<2)	xx	xx
Tetrachloroethylene (PCE)	0.969	0.59	0.973/0.990	1.20/1.19
1,1,1-Trichloroethane (TCEA)	0.989	0.37	0.991	1.16
Trichloroethylene (TCEE)	0.965	0.41	0.996	1.14
Vinyl Chloride	0.99	0.11	xx	xx

For chloride analysis by L2000DX, the analyte of each sample was extracted into 10 mL isooctane, followed by vigorous shaking for two minutes. The sample jars were then filled to zero headspace with deionized water, and the isooctane was allowed to settle in the neck of the bottle for at least three minutes. After the isooctane extract had settled, 5 mL were transferred into an L2000DX reaction tube. The samples were further prepared according to the instructions provided with the L2000DX instruction manual.[6] This preparation involved the complete isolation of chloride ions from the analyte.

The L2000DX instrument was calibrated with a standard 50 ppm chloride solution. Before the samples were tested, standard 10 ppm and 1000 ppm chloride solutions were checked. The chloride content of all samples were measured using the uncorrected L2000DX Chloride Method.

Initial preparation of samples for GC analysis was identical to that of the L2000DX samples. For the GC readings, however, the samples were injected into a purge-and-trap device after the chlorinated solvent had been gently mixed into the 965 mL of water. For analyte concentrations up to 2 ppm, 5 mL of sample were drawn into a syringe with a Luer-Lock connection without a needle. Into this solution, 5 mL of an internal standard was injected. The internal standard consisted of a 2000 mg/mL solution of 2-bromo-1-chloropropane and fluorobenzene in methanol. This combined solution with internal standard was injected into the purge-and-trap device. For 5 ppm and 10 ppm solutions, 1mL of sample was diluted to 5 mL with deionized water, then injected into the purge-and-trap along with 5 mL internal standard. The purge-and-trap served to extract all the low-boiling solvents out of the sample into the gas phase by bubbling an inert purge gas through the water. The analyte and internal standards were collected in the trap. After the purging was complete, all analytes that had collected into the trap were desorbed onto the GC column. A calibration curve of the analytes studied was made from 0.15 ppm to 2.0 ppm. The calibration curve and all samples were run using the EPA Volatiles 502.2 method.

PERC was additionally analyzed by GCMS, using EPA VOC Method 8260. The GCMS samples were also injected via purge-and-trap and most were diluted by a factor of 10 or 100, depending on the initial concentration of the samples. This method used an internal standard mixture of pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene at a fixed concentration reading of 50.00 mg/L. In the internal standard mixture, the surrogate analytes present were dibromofluoromethane, toluene-d_8, and 4-bromofluorobenzene at concentrations of approximately 100.0 mg/L. A calibration curve for PERC was made of concentrations ranging from 5 ppb to 200 ppb.

RESULTS AND DISCUSSION

The methylene chloride experiments indicate that varying water quality parameters have little effect on the recovery of chlorinated solvents. While this means that the recovery of methylene chloride cannot be easily improved, it also indicates that variations in ground water should not significantly affect recoveries in the field. As expected, pH did affect the recovery of PCP. The recovery improved from 54% to 60% when the pH was reduced from neutral to less than 2.

The one water parameter that did have an affect on recovery of chlorinated solvents was

temperature. Spiking water of various temperatures at 1 ppm with PCE resulted in recoveries ranging from 35% at 2 ºC to approximately 60-65% at 12 ºC. Above 12 ºC the recoveries remained more or less constant in the 60-70% range, up to the highest temperature tested at 45 ºC.

In order to determine the recoveries, theoretical corrections were made to the instrumental readings to account for percent chloride (on L2000DX readings only) and dilution/concentration factors. While the GC experiments analyzed the VOC analyte concentrations directly, the L2000DX uses a chloride-specific electrode, which measures free chloride concentration. The L2000DX readings were converted from chloride concentrations to analyte concentrations by dividing the measurement by the percent chlorine in the analyte. The extraction of the analyte from water to isooctane produced a size multiplier for the L2000DX samples of 965/10 = 96.5. Although there was no extraction involved in the GC samples, a size multiplier of 5 was used for the most concentrated samples since these samples were diluted by a factor of five. Similarly for GCMS samples, the dilution factor was the size multiplier. Once these theoretical corrections had been made, a regression analysis of the corrected instrument response versus the theoretical concentration for each analyte indicates the linearity of the response. Table 1 shows the comparison of the coefficient of regression for both the L2000DX and the GC/GCMS response curves. Figure 1, showing the measured concentration versus the theoretical concentration for PCE, illustrates a typical response curve for both methods. The slopes of the regression line can be taken as the average percent recoveries for each analyte, as shown in Table 2.

Figure 1: Recovery of PCE from Water (omitting 2 outliers)

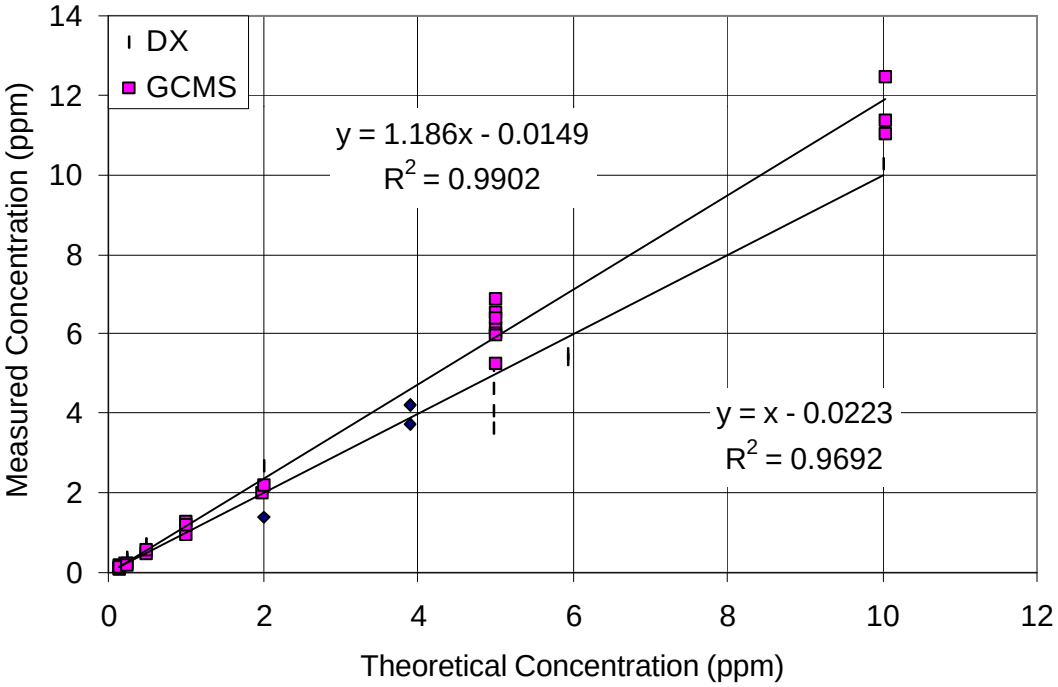


Table 2. Physical Data and L2000DX MDLs and Recoveries

Analyte	H_2O Sol. (wt %)	Typical Log K_{ow}	Recovery	Spike Level (ppb)	MDL (ppb)
Carbon Tetrachloride	0.08	2.6 (2.2-3)	0.58	51	16
1,2-Dichloroethane (DCEA)	0.81	1.5 (1.4-1.8)	0.18	250	71
cis-1,2-Dichloroethylene (DCEE)	0.35	1.7 (1.5-1.9)	0.26	xx	xx
trans-1,2-Dichloroethylene (DCEE)	0.63	1.9 (1.5-2.1)	0.41	xx	xx
1,2-Dichloroethylene (*cis*/*trans* mix)	xx	xx	0.26	150	86
Methylene Chloride	1.32	1.2 (1-1.5)	0.09	377	157
Pentachlorophenol (PCP)	0.008	3 (1.3-5.9)	0.54 (0.6@pH<2)	72	37
Tetrachloroethylene (PCE)	0.015	2.7 (2.4-3.4)	0.59	53	22
1,1,1-Trichloroethane (TCEA)	0.13	2.5 (2-2.6)	0.37	58	25
Trichloroethylene (TCEE)	0.11	2.3 (2-3.3)	0.41	63	23
Vinyl Chloride	0.88	1 (0.6-1.4)	0.11	207	94

A plot of the average recovery versus the analyte solubility in water for all analytes tested, indicates that the recovery is inversely proportional to an analyte's solubility (See Figure 2). Using published data, it can be seen in Figure 3 that a reasonable approximation of the recovery can also be made based on an analyte's octanol/water partition coefficient.[7]

Figure 2: Recoveries Vs Solubilities (all analytes)

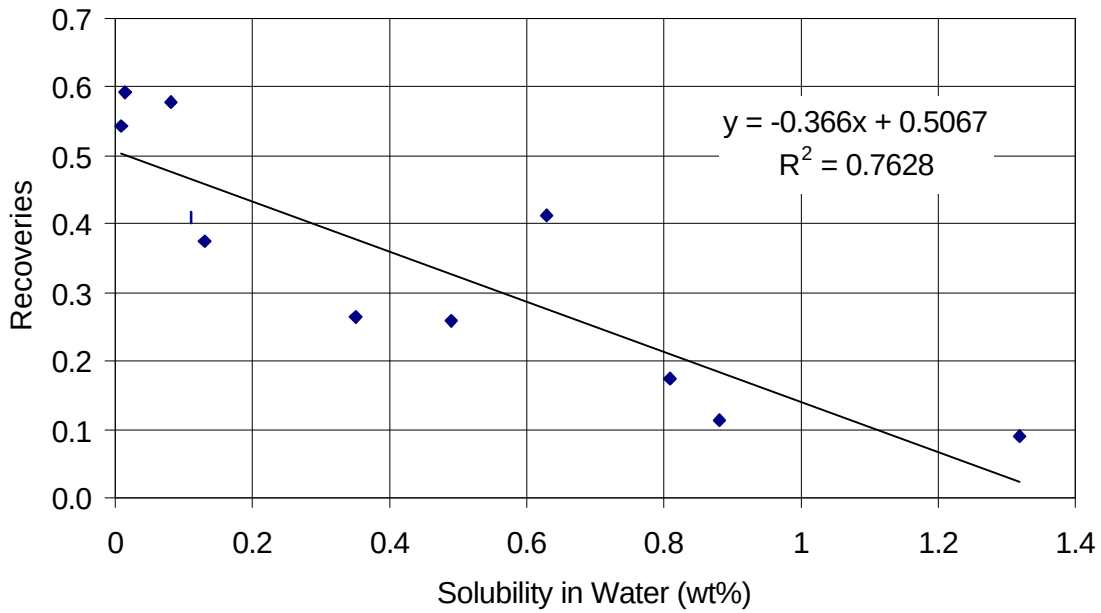
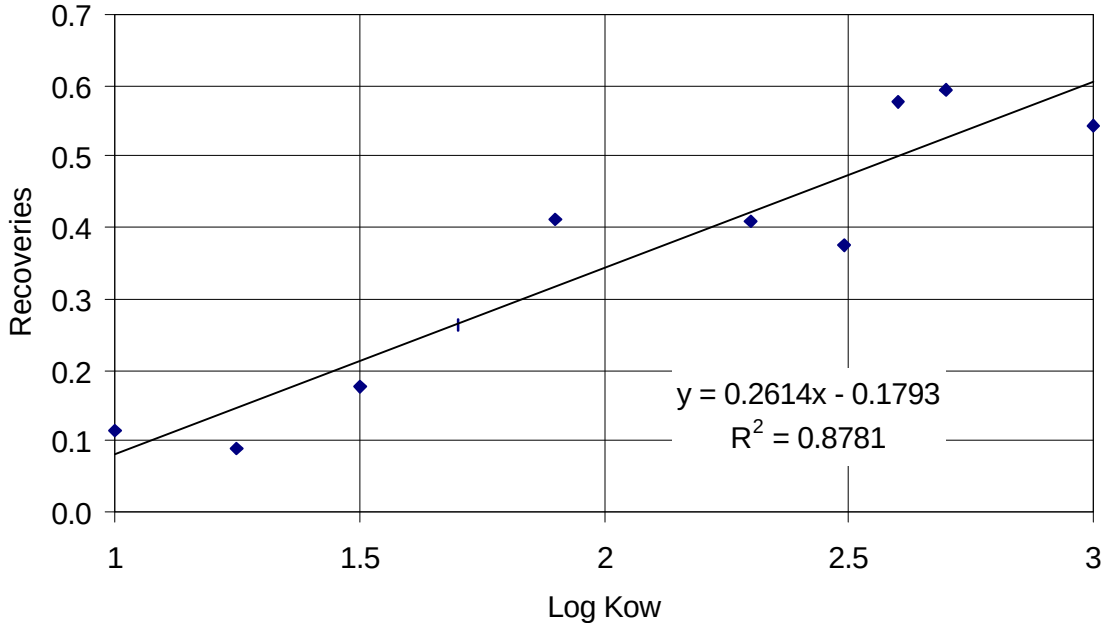


Figure 3: Recoveries Vs Log Kow (all analytes)



The ultimate sensitivity of the L2000DX method is determined by the sensitivity of the ISE. The practical limit for chloride detection, with some low-end corrections, is 1 ppm in the final extract solution used for quantification. Since all of the preparation steps are the same for each analyte, and the final extraction multiplier is determined by the extraction efficiency, the achievable MDL for each analyte will, therefore, be a function of the recovery. The results from the MDL determinations, listed in Table 2, confirm this general trend with the lowest MDL of 16 ppb achieved for carbon tetrachloride (58% recovery) and the highest of 157 ppb for methylene chloride (9% recovery).

SUMMARY

The results from the response range experiments indicate that the L2000DX liquid/liquid extraction method for water has a linear range up to 10 ppm for all of the analytes tested. The coefficient of regression was greater than 0.96 for all analytes including methylene chloride, the hardest to extract. The recovery for each of the analytes has been demonstrated to be consistent and reproducible enough to make this method a suitable method for field use. Typical MDLs are in the 25 ppb range for most of the analytes of interest which should make the L2000DX water method a useful tool for monitoring ground water in areas contaminated with chlorinated solvents. Now one instrument can be used to track contamination in both soil and water. This type of screening can be used for checking the progress of a treatment process, defining the limits of a contamination plume, as well as, monitoring ground water over long periods of time. All of these applications do not require expensive laboratory analysis and the L2000DX can provide the information in the field in 10 minutes.

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LOW LEVEL DETECTION OF PCE IN MONITORING WELL SAMPLES USING A TOTAL ORGANIC CHLORINE BASED FIELD METHOD

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ABSTRACT

Using the newly developed liquid-liquid extraction procedure for the L2000DX Chlorine Analyzer, Dexsil Corporation, in conjunction with Levine Fricke Recon (LFR), conducted a series of field trials at a tetrachloroethylene (PCE) contaminated site. The site chosen for the demonstration consisted of a network of monitoring and extraction wells located in a PCE plume impacting ground water.

The new procedure is an addition to the existing methods for the L2000DX Chloride Analyzer which is the basis for SW-846 Method 9078 "Screening Test Method for Polychlorinated Biphenyls in Soil." Using the same reaction and quantification steps as the established L2000DX methods, the new method uses a liquid-liquid extraction step to achieve MDLs in the 15-30 ppb range for most chlorinated solvents. The MDL for PCE using this method is 22 ppb. This new method will allow nearly real time data to be collected from ground water monitoring wells at a fraction of the cost of laboratory analysis.

The field trial was conducted in two phases. Each phase was planned to coincide with the normal monitoring activities at this site. During the sampling operations, split samples were taken to be analyzed by the L2000DX at the field location. The laboratory samples were sent off to the state certified lab, as usual, for analysis by SW-846 Method 8260A. A total of 17 monitoring wells were sampled for a total of 26 samples and 12 duplicates. The L2000DX results were available the same day as the sampling event. The PCE concentration in the samples ranged from non-detect to greater than 20 ppm, providing a good sample set to test the comparability over a large concentration range.

A regression analysis of the data set indicates that the L2000DX results compare very well with the lab results over the full range. The excellent correlation between the L2000DX results and the lab results, (R^2 = 0.99), indicates that the field method provides data comparable to the laboratory in practically real time. This field trial demonstrated the utility of a total halogen based field method for ground water monitoring of PCE contamination.

INTRODUCTION

Regulatory driven quarterly monitoring is a common event at sites where groundwater is contaminated by chlorinated organic compounds. The objective of quarterly monitoring is to determine the concentration of a contaminant in the water from established monitoring wells over time. The data are then examined and seasonal changes and overall plume trends can be evaluated quarterly.

The conventional protocol for quarterly monitoring consists of collecting water samples from monitoring wells and sending them to a certified analytical laboratory for analysis. This conventional "sample and send" method may not be justified when the purpose is to monitor the clean-up of known contaminants over decades. A low cost accurate field analytical test kit is essential for sites like these that require long term monitoring. A sample for laboratory analysis can be collected when contaminant concentrations indicated by the field test data are at or near actual clean-up concentrations, when an anomaly is detected by the field analysis or as a quality assurance step for a field test.

If extraction wells and a remediation system are added to the site, the quarterly monitoring data is also studied to determine changes in plume dynamics as well as expected changes in contaminant concentrations at each monitoring well over time. At sites where a remediation system is in place, a low cost field analytical test kit should be considered as an alternative to the conventional "sample and send" to the laboratory protocol.

Sites contaminated with a dense non-aqueous phase liquid (DNAPL) in either the vadose zone, or groundwater, are difficult to assess due to the fact that DNAPLs react differently than light non-aqueous phase liquids (LNAPLs) do in the subsurface. Both will move through the vadose zone and can dissolve into groundwater forming a contamination plume that will move and expand in the direction of groundwater flow, but DNAPLs will continue to move down through groundwater and form pools of DNAPL that can then be a continuous source of groundwater contamination or continue to move downward eventually contaminating deeper aquifers. These DNAPL pools are difficult to locate using conventional methods and are often the reason these types of sites may require long-term quarterly monitoring and long-term remedial efforts. The use of a field analytical test kit at long term monitoring sites provides better site control, while saving time and financial resources.

In response to the demand for a field test kit for water, Dexsil has developed a new extraction method for use with the L2000DX Chlorine Analyzer. The new procedure uses a liquid/liquid extraction to concentrate organo-chlorine contaminants into an organic layer for introduction into the L2000DX system. The L2000DX chemistry then uses metallic sodium to convert all of the organic chlorine into chloride for quantification by chloride ion specific electrode. The L2000DX system has been shown to be a reliable platform for chloride analysis through the USEPA SITE and ETV programs.[1,2] The new procedure and the laboratory development of the extraction step is detailed in a concurrent paper.[3]

After laboratory testing of the new method, Dexsil teamed up with Levine-Fricke-Recon (LFR) to conduct field trials at a real world site. LFR, a leader in the use of innovative environmental technology, was aware of the need for an accurate, low cost, quantitative field test kit for use at sites where chlorinated compounds are contaminating groundwater. Also interested in the potential for saving its client’s long-term costs at DNAPL sites, LFR suggested a site where they had been implementing a system of monitoring wells for a quarterly monitoring program. Previous monitoring activity had documented the presence of tetrachloroethylene (PCE) at concentrations of up to 30 ppm in some wells.

This paper describes the field testing activities, conducted jointly by LFR and Dexsil personnel, comparing the L2000DX Analyzer to laboratory analysis. The sampling was

conducted in two separate three-day events, the first in November of 1998 and the second in February of 1999.

SAMPLING AND ANALYSIS

The site chosen for the field trials encompasses a large downtown retail area with a network of monitoring wells and extraction wells located throughout. The sampling activities planned for this study were scheduled to coincide with the scheduled quarterly sampling of the monitoring wells and were performed by LFR personnel. Most of the sampling was performed after 8:00 pm to avoid a conflict with active businesses located on or in the vicinity of the site. All water samples, upon collection, were immediately stored in coolers containing crushed ice. The samples that were collected for laboratory analysis were placed into a separate cooler from those collected for field analysis and a courier for the laboratory picked them up each morning. Dexsil also picked up the corresponding field test samples each morning. Each water sample was collected using accepted EPA methods. The laboratory samples were collected in 40mL VOA vials preserved with HCl and collected to zero headspace. The samples for field analysis, requiring a liter of sample with no preservative, were also collected to zero headspace. Dexsil personnel analyzed each sample and duplicate samples the day they were collected. The analysis time per sample using Dexsil's L2000DX analyzer was approximately 10 minutes per sample. Dexsil requested that duplicate samples be collected whenever possible. Dexsil personnel had ample time to analyze trip blanks, spikes and duplicate samples each day. Dexsil analyzed a total of 50 samples; 12 of them were duplicates, eight were spikes and four were trip blanks.

The L2000DX analysis procedure used for this study consisted of a liquid/liquid extraction using 10 mL of 2,2,4-trimethylpentane (isooctane) followed by the standard L2000DX analysis procedure. To begin the analysis, 40 mL of water was removed from the cooled, zero headspace sample. This left 960 mL in the sample jar with enough headspace for extraction. 10 mL of isooctane was added and the sample was shaken by hand for 2 minutes. After extraction, sufficient deionized water was added to the sample jar to bring the organic layer up into the neck of the jar. The sample was allowed to sit capped for three minutes. 5 mL of the organic layer was then removed and introduced into the standard L2000DX sample tube. The standard procedure was then followed according to the instruction manual.[4]

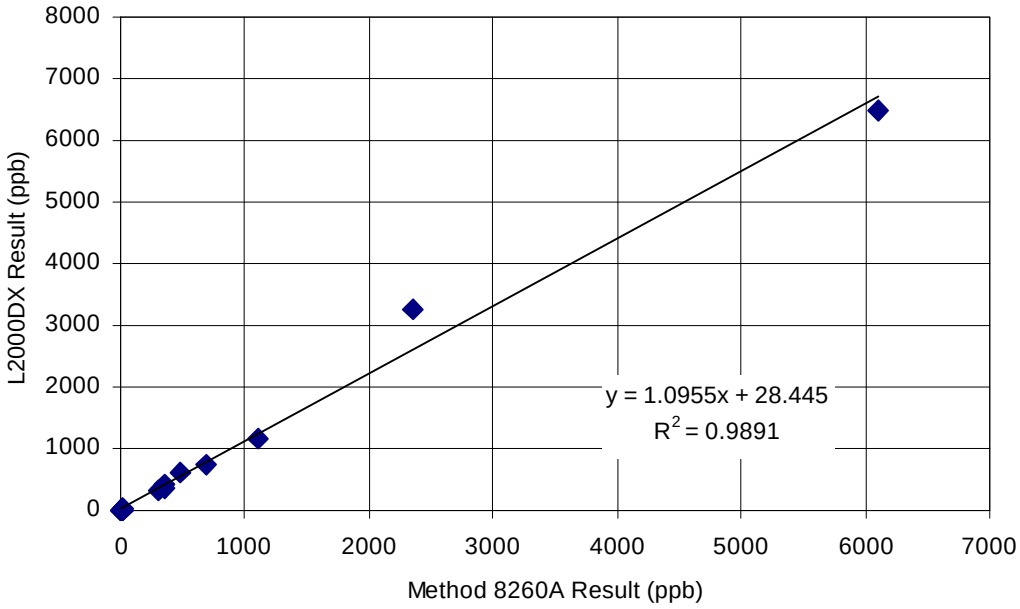
RESULTS AND DISCUSSION

All of the water samples collected during this comparative study were sent to a certified laboratory and were analyzed using EPA SW-846 Method 8260A. The laboratory results were available four (4) weeks after the samples were sent in. In contrast, the analytical results for each of the corresponding water samples analyzed using the L2000DX analyzer were available the same day and in some cases, hours after they were received. At the conclusion of each three-day round of field testing, Dexsil faxed the analytical results from the on-site L2000DX testing to LFR.

Initial analysis of phase I data resulted in a correlation coefficient of 0.982 but a regression slope of only 0.6. This would indicate only a 60% recovery. This would be unlikely because the L2000DX software has a correction for extraction efficiency built into each method. Further investigation indicated that the regression was strongly influenced by sample MW-006A. The laboratory result for this point was 39 ppm whereas the L2000DX result was

only 23.4 ppm. Subsequent laboratory experiments revealed that the linear range for the extraction procedure extends only to approximately 20 ppm, after which the solvent becomes saturated. Removing point MW-006A from the analysis results in an R^2 of 0.989 which is not much different but the slope becomes 1.1 indicating the L2000DX results correlate well with the lab and the slope is not statistically different from 1 (See Figure 1).

Figure 1: L2000DX vs Lab for PCE Analysis of Water Phase I (outlier removed)



Analysis of the duplicate sample results indicates that the L2000DX produces very consistent results with an average RPD of 7.1% for the five duplicates for which valid results were obtained. NOTE: Results for samples MW-002A, MW-009A and MW-104A and their duplicates were non-detect (ND) and, therefore, could not be used to calculate an RPD. In addition, during the processing of sample MW-010A-D, some of the extraction solvent was lost after the chloride conversion, possibly lowering the result. This point was not used to calculate the average RPD (See Table 1).

Table 1. Comparison Data for Phase I and Phase II Testing

Sample ID	Phase I			Phase II	
	Method 8260A Result (ppb)	L2000DX Result (ppb)	L2000 RPD	Method 8260A Result (ppb)	L2000DX Result (ppb)
MW-001A	ND (7.2)	ND (9.8)			
MW-002A	ND (7.9)	ND (7.4)		7.19	ND (12.3)
MW-002A-D	ND (8.3)	ND (9.7)			
MW-003A	350	339	6.39	1400	2104
MW-003A-D		318			
MW-004A	1100	1168		1130	1262
MW-005A	17	40.5	14.3		
MW-005A-D		35.1			
MW-006A	39000	23445	4.2	21196	26880*
MW-006A-D		22481			29920*
MW-007A	480	608	8.2	445	468
MW-007A-D		660			
MW-009A	11	ND (18.8)		9.3	ND (11.2)
MW-009A-D	14	ND (20.8)			
MW-010A	360	407		8.9	30.3
MW-010A-D		327†			
MW-101A	6100	6484		6831	6150*
MW-101A-D		6329			
MW-104A	ND (12.8)	ND (13.4)	2.42		
MW-104A-D	ND (12.5)	ND (14.8)			
MW-108A	2360	3254		2051	
MW-109A	307	309		58.8	143
MW-113A				7	ND (11.2)
MW-113A-D					ND (4.1)
MW-205B	691	742		735	
MW-209B	5.6	12.7			
MW-210B				4	ND (0)
MW-210B-D				4.9	ND(4.7)
SPIKE		1601			1494
SPIKE		1739			1519
SPIKE		1701			1851
SPIKE		1419			1935
TRIP BLANK		ND (0.8)			ND (7.9)
TRIP BLANK		ND (0.8)			ND (1.1)

* High range procedure used

Between phase I and phase II, the analysis protocol was modified to include a re-analysis of high samples using a reduced sample size. This was easily accomplished by using the 40 mL removed from the sample at the start of the analysis as a laboratory split sample and extracting this sample for later analysis, if the initial analysis is high. Samples MW-006A, MW-006A-D and MW-101A from the second round of sampling were analyzed and reported using this method.

The analysis of phase II data resulted in an R^2 of 0.991 and a slope of 1.24 indicating a slightly elevated recovery (See Figure 2). Again, the regression is influenced by the one high data point, elevating the slope. An analysis of all the data (excluding MW-006A) results in an R^2 of 0.990 and a slope of 1.23 (See Figure 3). Excluding points greater than 10 ppm results in a slope of 0.996 and an R^2 of 0.977 (See Figure 4).

Figure 2: L2000 vs. Lab for PCE in Water (Phase II)

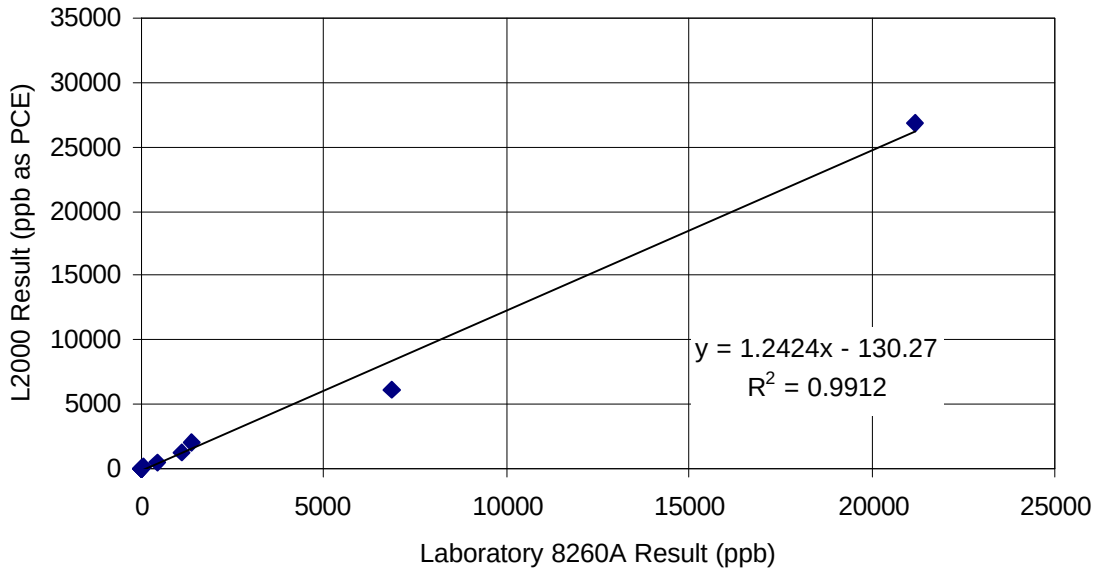


Figure 3: Comparison Data PCE in Water (All Data except MW-006A Phase I)

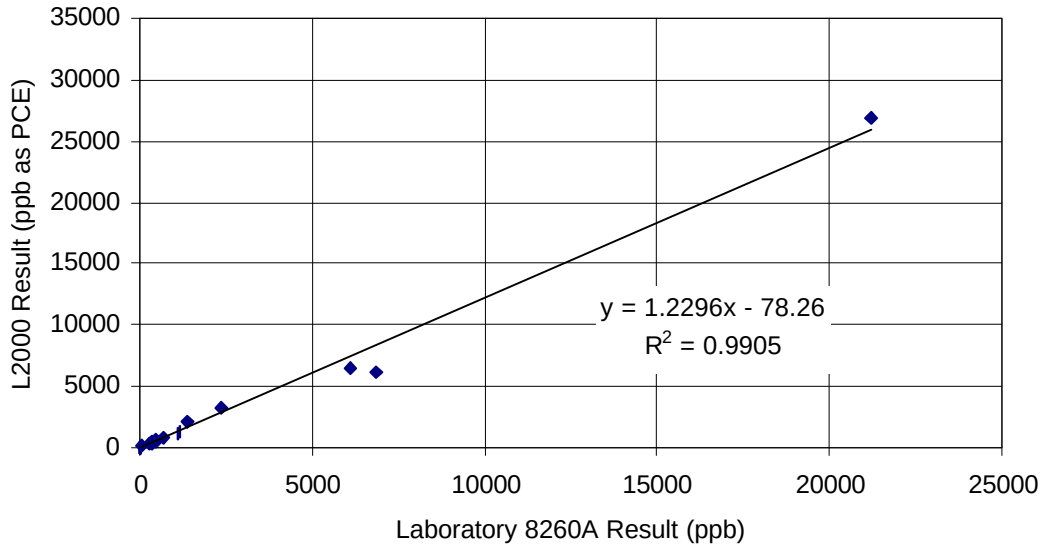
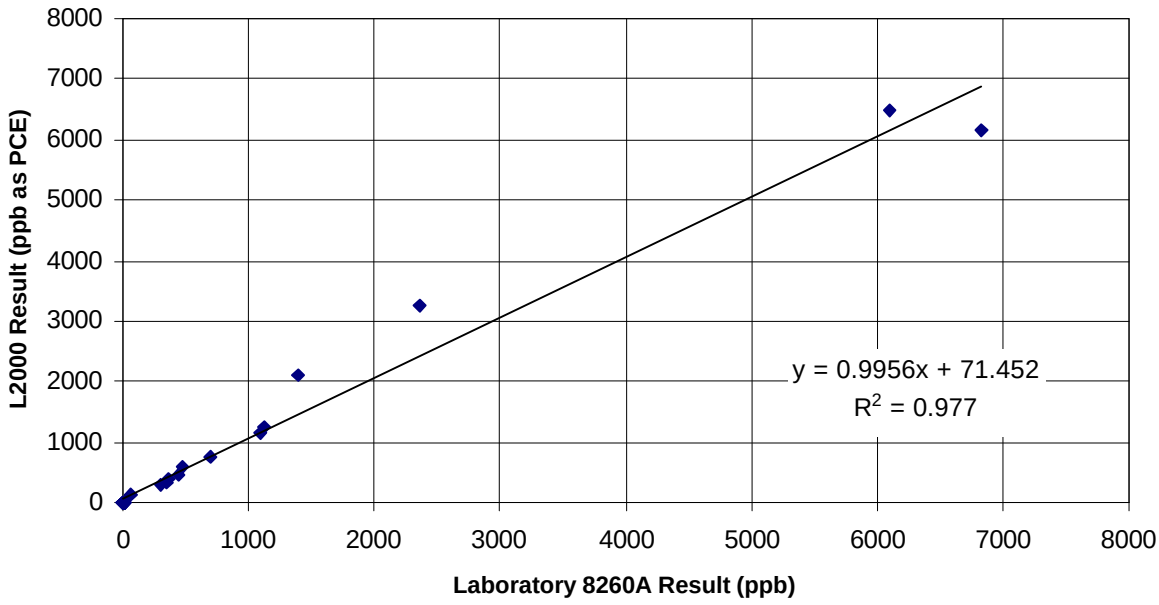


Figure 4: Comparison Data for PCE in Water (All data points less than 10 ppm)



As part of the field QA/QC program, Dexsil also analyzed 8 spiked samples and 4 trip blanks. The spikes were made in chilled water at 1657 ppb. The results shown in Table 1 indicate a good spike recovery ranging from 89% to 117% with an average recovery of 102%. All four trip blanks tested ND.

SUMMARY

During this comparative study, a total of 17 monitoring wells were sampled. This resulted in a

total of 31 water samples being sent to a laboratory for analysis by US EPA SW-846 Method 8260A, and 38 samples were analyzed using Dexsil Corporations' L2000DX Analyzer Field Test Kit method. The analytical results of both the field test and the laboratory analysis were compared directly. The correlation was excellent (R^2 = 0.990) when all the data were compared. Dexsil's L2000DX Analyzer proved to be an easy to use, low cost and accurate field analytical test method. In addition to the excellent correlation with lab samples, the low cost of the test (less than $10 per test versus $200 for an 8260A) coupled with near real time results makes the L2000DX an excellent alternative to laboratory analysis at sites where water is contaminated with PCE or other DNAPLs. The L2000DX can replace the conventional method of "sample and send" with an on-site field analytical test kit. At the beginning of a project, a few samples must be sent to a laboratory for characterization. Once sample characterization is complete, the L2000DX Analyzer is easily programmed for the site-specific contaminant. After this initial characterization is complete, the L200DX should be used exclusively to analyze water samples at the site. Prudence dictates that an occasional random sample should be sent to a laboratory for analysis by the appropriate method to confirm correlation with the field method.

Quarterly monitoring and site investigations are expensive, and using the conventional "sample and send" protocol does not make economic sense based upon the benefit derived verses the cost of the lab data. New strategies for site assessments, long-term monitoring and site remediation need to be considered for DNAPL sites due to the problems they present when discovered. Dexsil's L2000DX is an important and significant new field test kit that environmental professionals can use to improve site assessments. The use of the L2000DX Analyzer at a wide variety of DNAPL sites will aid in facilitating and directing site assessment strategies, save time and money and save long-term costs and overall project costs significantly.

ACKNOWLEDGMENTS

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ASSESSMENT OF THE EFFECTS OF ACTIVE SITES IN DISCRETE SAMPLING, PURGE AND TRAP CONCENTRATORS ON OXYGENATED COMPOUNDS

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ABSTRACT

Active sites, which are a common problem encountered during analysis by gas chromatography, are most commonly associated with the column and sample inlet on the gas chromatograph. The effects of active sites in these areas are easy to observe, as they will affect every analysis in a sequence. The analysis of volatile organic compounds using discrete sampling purge and trap concentrators presents a more interesting and currently relevant challenge as they are sometimes overlooked as potential locations of active sites. Several discrete sampling systems that are widely used in commercial laboratories consist of sixteen individual sampling locations, each with its own electroform nickel sample pathway plumbed into a multi-position valve. When an individual sample pathway develops an active site or becomes contaminated, the effects are observed only on samples analyzed at the affected position, not uniformly at all sampling positions. This problem makes identifying active sites extremely difficult if each sampling position is not monitored for this phenomenon.

The authors observed this phenomenon while validating a large data set that was analyzed over a period of several months. At least one, and possibly more, sample positions displayed an active site that had a negative impact on the detection of the target compounds methyl *tert*-butyl ether, ethyl *tert*-butyl ether, *tert*-amyl methyl ether and *tert*-butyl alcohol; however, the target compounds diisopropyl ether, benzene, toluene, ethylbenzene, *m*+*p*-xylenes and *o*-xylene were not affected. A contributing factor to the difficulty encountered in discovering this phenomenon was that the accompanying surrogate and internal standards were not affected. The effects of the active site were only observed when either a calibration standard or a laboratory control sample was analyzed at sample positions in question.

The research presented herein will discuss the potential impacts of false negatives by position-specific active sites, how this phenomenon was observed, the difficulties in identifying the relevant affects on specific samples and recommendations for identification of these active site problems on a commercial laboratory production basis.

INTRODUCTION

A problem commonly encountered during the analysis of samples using gas chromatography is the development of active sites within the analytical system. Active sites are commonly found on the silicate surfaces of capillary column walls, column packing and sample inlets/injection port liners. These active sites result in the physical adsorption of polar or polarizable compounds. This affinity for polar compounds is the result of silanol (Si-OH) and

siloxane (Si-O-Si) groups that form on the surface of the active site. These groups offer two different paths to hydrogen bonding. The silanol group acts as a proton donor and the siloxane group acts as a proton acceptor. Another potential problem with active sites is the presence of mineral impurities, such as iron and aluminum oxides, that can catalytically degrade certain compound species.

The effects of active sites in the column or sample inlet are relatively easy to observe as their affects would be observed in every analysis in a given sequence. This is obvious in that every sample must travel through the same sample inlet and column; therefore, active sites in either of these areas would affect all analyses. The analysis of volatile organic compounds using discrete sampling purge and trap concentrators presents an interesting challenge as they are sometimes overlooked as potential locations of active sites. Several discrete sampling systems that are widely used in commercial laboratories consist of sixteen individual sampling locations where each sample is held in its own discrete sample tube. Each of the individual sample locations is plumbed with its own electroform nickel sample pathway that connects to a multi-position valve. In this sample pathway, the gaseous form of the sample comes into direct contact with the tubing. Over time, the electroform nickel tubing ages and active sites develop, resulting in breakdown and/or adsorption of certain analyte species. When an individual sample pathway develops an active site or becomes contaminated, the effects are observed only on samples analyzed at the affected sample location, not uniformly at all sampling positions. An active site in an individual sample pathway may be less obvious and extremely difficult to identify, especially if each sampling position is not monitored for this phenomenon.

The authors observed this phenomenon while validating a large data set of samples that were analyzed over a several month period at a commercial laboratory using one particular sample concentrator and instrument. This large amount of data over a long period of time enabled the authors to detect a trend with at least one, and possibly more, sample positions where an active site negatively impacted the analysis of methyl *tert*-butyl ether, ethyl *tert*-butyl ether, *tert*-amyl methyl ether and *tert*-butyl alcohol. The recoveries of benzene, toluene, ethylbenzene, *m*+*p*-xylenes, *o*-xylene and diisopropyl ether at these affected positions were not impacted. A contributing factor to the difficulty encountered in discovering this phenomenon was that the accompanying surrogate and internal standards, none of which are oxygenated, were not affected. In order to observe the effects of the active site, a calibration standard or a laboratory control sample containing the target oxygenate compounds would have to be analyzed at each sampling location.

As mentioned previously, the polarity of the target compounds is directly responsible for whether or not they are affected by an active site. For a compound to be polar, there must be at least one polar bond or one lone pair of electrons **and** the polar bonds; if more than one, cannot be so symmetrically arranged such that the bond polarities cancel each other out. The reasons why some compounds are affected while others are not can be found by looking at the structures of the target compounds (See Figure 1). Benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene and *o*-xylene are all aromatic hydrocarbons and do not have the lone electron pairs necessary to be polar compounds. MTBE, ETBE, TBA and TAME all have two lone electron pairs on the oxygen and are not symmetrically arranged; therefore, both criteria for polarity have been met for these compounds. While DIPE is an oxygenate and thus has

two lone electron pairs on the oxygen molecule, the symmetry of the structure cancels out the polarity, and therefore fails one of the necessary criteria for determining compound polarity. Therefore, since the polar compounds MTBE, ETBE, TBA and TAME are the only compounds affected, the nature of the observed phenomenon fits the description of a common active site with an affinity for polar compounds.

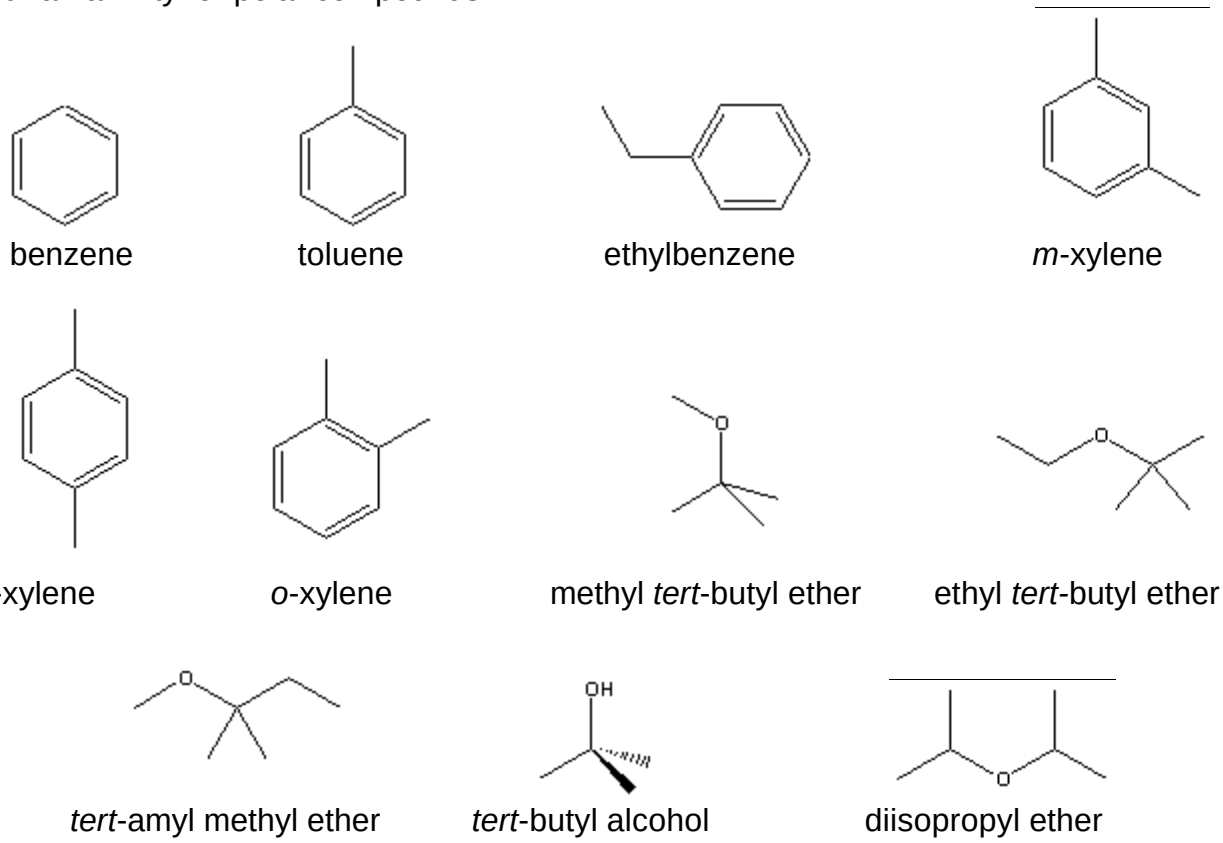

Figure 1.

DISCUSSION

During the validation of a large data set, the authors observed that the compounds methyl *tert*-butyl ether, ethyl *tert*-butyl ether, *tert*-amyl methyl ether and *tert*-butyl alcohol were consistently and totally "disappearing" from standards and/or quality control (QC) samples analyzed at one particular autosampler position in the analytical sequence. "The results of various tests involving spiking actual samples and QC samples with target analytes or similar non-target analytes (surrogates, internal standards, etc.) are used in evaluating the potential loss and/or degradation of various environmental contaminants from a sample during preparation or analysis at the laboratory" (Clark, 1996). Upon further inspection of the available data, the QC samples analyzed at another autosampler position displayed very low responses for the aforementioned compounds. In several cases, QC samples that were affected by the active site were reanalyzed at a different autosampler position immediately following the affected analysis using the same spike standard solution that previously displayed compound loss. In addition, these same "disappearing" oxygenate compounds were detected in standards analyzed at several other positions on the aforementioned instrument. This documented observation of the correctness of the standard clearly indicated that there

was not a problem with the standard used or with the system as a whole, nor was it the result of a bad purge as the internal standards, surrogate compounds and other target compounds were not affected.

The first indication that there was a potential problem with position-specific active sites was observed by the authors when verifying the initial calibration. The laboratory analyzed two separate initial calibrations to include all project specific target compounds. The first initial calibration (MBTEX) contained the compounds benzene, toluene, ethylbenzene, *m*+*p*-xylenes, *o*-xylene and methyl *tert*-butyl ether (MTBE). The second calibration (Oxygenate) contained MTBE, ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE) and *tert*-butyl alcohol (TBA). (While MTBE was included in both the MBTEX and Oxygenate initial calibrations, results for MTBE were quantitated using the MBTEX initial calibration.) The MBTEX initial calibration was performed first. The large number of standards used in the initial calibration resulted in standards being analyzed on ten of a possible sixteen autosampler positions. The standards analyzed at the seventh and eleventh positions **(assuming the BFB tune is the first position)** did not display any response for MTBE. The instrument was then re-tuned and the Oxygenate initial calibration was performed. Like the MBTEX initial calibration, the standard analyzed at the seventh position did not display any response for MTBE, ETBE, TAME or TBA, yet DIPE and the non-oxygenated surrogate and internal compounds showed no signs of reduced or missing responses. Because a fewer number of standards was used in the Oxygenate initial calibration, an Oxygenate standard was not observed to be analyzed at the eleventh position. In both cases, the laboratory simply did not include a relative response factor for the missing compounds while including the relative response factors for the compounds that were detected in the standards. No explanation was provided by the laboratory as to why these points were dropped from the middle of these initial calibrations. At this point, it appeared to the authors that the laboratory did not take corrective action for the autosampler position, probably because the laboratory personnel did not recognize the phenomenon nor that it was happening consistently at the same autosampler positions.

The authors then examined all standards and QC samples analyzed at the aforementioned positions and observed the same phenomenon. The specific types of samples analyzed at each autosampler position limited this examination. Due to the nature of the active site, the surrogate compounds dibromofluoromethane, toluene-d_8 and bromofluorobenzene, and internal standard compounds pentafluorobenzene, 1,4-difluorobenzene and chlorobenzene-d_5 were not affected; therefore, unless a standard or QC sample containing the affected oxygenate compounds was analyzed, it was impossible to positively determine that a particular position was affected or not. Several standards and QC samples were analyzed at the seventh position that displayed consistency over time; however, consistency could not be established for the eleventh position because only one standard was available to evaluate.

During the examination, the authors observed that many project samples were analyzed on the affected positions. Because the contents of the samples were unknown, the specific effects of the active sites on the project samples are also unknown. One potential indicator was that throughout the data examined, a consistent background level of TBA was observed in the majority of method blanks and samples analyzed on the particular instrument in question. In addition, high recoveries for TBA were also observed in the laboratory control

samples (LCS) and associated matrix spike/matrix spike duplicates analyzed on the particular instrument in question. Since the background TBA concentration level was fairly consistent, sample positions where TBA was not observed or was observed only at trace levels were considered to potentially be affected by active sites.

Several difficulties were encountered while evaluating the effects of the known and potential active sites, some of which have been previously discussed. From a data quality standpoint, known standards were either not analyzed or were not analyzed at a great enough frequency to evaluate the potential for this problem to exist at the positions used for method blank and sample analyses. Therefore, the authors did not have sufficient information to evaluate the potential problem as it would relate to the positions used for method blank and sample analyses. Adding to the problem was the fact that the laboratory did not maintain documentation as to which position was used for each sample analysis.

RECOMMENDATIONS

Based on an extensive review of affected data and available information related to the effects of active sites on the polar oxygenate compounds, the authors have formulated recommendations to help commercial laboratories identify and/or correct the problems created by the development of active sites within discrete sampling purge and trap autosamplers. In terms of stake-holding data users, these same recommendations can be used to identify these problems in order to properly assess defensibility (*e.g.*, legal proceedings) and usability of data. “Analytical data is the basis for determining many important factors such as contaminant source delineation, vertical and horizontal distribution of contaminants, human health risk and ecological impacts, and remedial alternatives. Given the significant economic costs to industry and taxpayers alike, the quality of the analytical data to these processes is extremely important” (Blye, 1995).

In order to be aware of the possible effects of position specific active sites, it is important to clearly document at which autosampler position a particular sample or standard is analyzed. Along with tracking positions, it is equally important to monitor each sample position by analyzing a standard or laboratory control sample at each position over time. For example, if the same five sample positions are used in the analysis of initial calibrations, continuing calibrations and QC samples, only those five positions can be effectively monitored for potential active sites. This is as easy as using five different positions from those used for the previous initial calibration. With this information, analysts can monitor reductions in specific compound recoveries as well as specific compound loss and have the information needed to easily identify at which sample position there is a problem.

A significantly more effective and real-time recommendation for identifying active sites with an affinity for polar compounds in specific autosampler positions is to include an additional surrogate and/or internal standard compounds that more closely match the characteristics of polar compounds. None of the surrogate or internal standard compounds recommended in US-EPA SW-846 Method 8260B act as polar compounds and, as previously mentioned, are not affected by these active sites. Ideally, the authors recommend the use of both a polar surrogate **and** internal standard compound when the target compound list includes polar compounds such as the aforementioned oxygenated compounds; however, if only one is to be used, it should be the internal standard. The internal standard is added to all samples and

standards at the same concentration regardless of dilutions or other sample preparation events, which is not always the case for surrogate compounds. The authors recommend the use of deuterated *tert*-butyl alcohol (*viz*., TBA-d_{10}) as an internal standard. This will allow for a degree of monitoring in project samples that are not spiked or otherwise monitored for loss of polar compounds.

Should a laboratory encounter an autosampler position-specific active site, there are corrective actions that can be taken. One leading manufacturer suggests acid purging the nickel tubing to passivate these active sites. Specific directions on this procedure can be obtained from the autosampler manufacturers. As previously mentioned, as the nickel tubing ages, primarily from the hydrochloric acid used to preserve aqueous samples, it is more likely to develop active sites. Therefore, once an active site has developed, even if passivated by acid purging, it is likely that more active sites will be encountered in the future. The authors recommend replacing the affected nickel tubing, which should greatly increase certain compound sensitivities and prevent the recurrence of these active sites for a longer period of time.

CONCLUSION

In conclusion, laboratories and stake-holding data users should be aware that autosampler position-specific active sites encountered during the analyses of volatile organic compounds using discrete sampling, purge and trap concentrators are common and are very difficult to detect if proper measures are not taken. These measures include tracking at which position each sample or standard is analyzed, analyzing known concentration standards or QC standards at each position over time, and using polar surrogate and internal standard compounds when the target compound list includes polar compounds. This phenomenon can result in reporting false negatives that can go undetected until the phenomena is discovered during a third-party data review performed by credentialed, experienced chemists. “Even when not required by a regulatory agency, validation of analytical data is frequently sought by investigators when environmental results have significant implications such as high expenses/fines or complicated treatment” (Clark, 1996). Such observations will result in data that cannot be defended for important decision-making processes.

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EFFECTS OF PURGE AND TRAP INJECTION TECHNIQUES ON CHROMATOGRAPHY PEAK SHAPE

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In an effort to increase throughput and sensitivity, peak shape has become a major focus for gas chromatographic methods. Improving peak shape has a direct effect on the quantitation as well as the resolution of complex mixtures. Sharper peaks yield lower detection limits as well as faster GC run times. When a volatile introduction system is incorporated in the chromatography system, peak shapes can suffer due to the additional dead volume.

Several injection techniques have been developed to improve peak shapes when volatile introduction systems are used. In this paper, the research will identify injection techniques that can be used to improve chromatographic peak shapes when a purge and trap system is used as the sample introduction device. Methods such as cryogenic trapping and split flows will be evaluated to show their effects on peak shapes.

The parameters evaluated for their effect on chromatography are as follows:

I. Split Flows A. Splitless B. Split 1. 10:12. 20:13. 40:1	I. Split Flows A. Splitless B. Split 1. 10:12. 20:13. 40:1	II. Turbocool Option A. Splitless B. Split 1. 10;12. 20:13. 40:1	III. Cryofocusing Option

Split inlets allow splitting of a sample as it transfers from the concentrator to the column. Although a large amount of sample mass is lost through the split vent, the improved signal-to-noise ratios actually increase sensitivity.

The Turbocool option involves cryogenically cooling the adsorbent trap with liquid carbon dioxide. Without splitting the sample, Turbocool offers a slight improvement in peak shape since migration of the more volatile components through the trap is inhibited at subambient temperatures.

One advantage in having Turbocool installed is that it promotes very rapid cooling of the trap.

The cryofocuser module refocuses the analytes onto the head of the column during desorption as a very narrow plug. The biggest disadvantage with cryofocusing involves the expense and special handling requirements of liquid nitrogen.

In the data shown in this paper, the methanol interference could not be eliminated since a FID was used as the detector. But if a mass spectrometer is used as the detector, similar peak shapes will be observed. The solvent contribution can be removed with a solvent delay and scanning above mass 32.

All three techniques presented in this paper can provide excellent chromatographic peak shapes. Reproducibilities and linear responses are generally comparable among these techniques as well at low to mid-ppb levels.

Example Reproducibilities (%RSDs for n=7 runs)
Benzene (Split 10:1, 1.97%; Turbocool, 3.31%; Cryofocusing, 2.80%)
Toluene (Split 10:1, 1.96%; Turbocool, 2.65%; Cryofocusing, 2.75%)
Ethylbenzene (Split 10;1, 1.66%; Turbocool, 1.61%; Cryofocusing, 3.74%)
Xylene (Split 10:1, 1.50%; Turbocool, 2.69%; Cryofocussing, 3.12%)

Example Linearities, 10-60 ppb (triplicate runs)
Benzene (Split 10:1, 0.9992; Turbocool, 0.9975; Cryofocusing, 0.9997)
Toluene (Split 10:1, 0.9990; Turbocool, 0.9985; Cryofocusing, 0.9984)
Ethylbenzene (Split 10:1, 0.9978; Turbocool, 0.9973; Cryofocusing, 0.9975)
Xylene (Split 10:1, 0.9947; Turbocool, 0.9954; Cryofocusing, 0.9967)

CRITICAL ANALYSIS OF USEPA METHOD 5035 USING A ROBOTIC VIAL AUTOSAMPLER

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In today's laboratories, increased efficiency and productivity are of extreme importance. Equally important is the ability to automate analyses without sacrificing sample integrity or data quality. The SOLATek 72 vial autosampler fully automates purge and trap analysis of water, wastewater and solids samples in accordance with current USEPA methods for volatile analysis.

Research will demonstrate the use of this robotic vial autosampler following USEPA 5035 sample preparatory protocol for the analysis of USEPA Method 8260 analytes.

The pertinent features of the SOLATek 72 will be described and all data will be evaluated for linearity and reproducibility.

Features unique to the SOLATek 72 include:

- 72 positions for 40-mL VOA vials
- 1-mL to 25-mL sample aliquots in 1-mL increments
- Incremental dilutions as low as 1:250
- Up to 3 standard injection systems
- Capacity up to 25 µL in 5 µL increments
- Silcosteel treated sample pathway
- Vial heater range: 30°C to 100°C
- Teklink software for integrated control
- One sequence can run both water and soil methods
- Three-axis linear motion robotic arm with linear slides, stepper motors and optical encoders

Precision of the internal standards and surrogates was evaluated on the basis of seven replicate data runs.

Internal Standards/Surrogates

Water Mode

Internal Standards: Fluorobenzene (2.35%), Chlorobenzene-d_5 (2.19%), 1,4-Dichloroethane-d_4 (2.50%).
Surrogates: Dibromofluoromethane (3.38%), 1,2-Dichloroethane-d_4 (2.14%), Toluene-d_8 (2.66%), 4-Bromofluorobenzene (3.47%).

Soil Mode

Internal Standards: Fluorobenzene (4.19%), Chlorobenzene-d_5 (3.59%), 1,4-Dichloroethane-d_4 (2.96%).
Surrogates: Dibromofluoromethane (4.35%), 1,2-Dichloroethane-d4 (2.59%), Toluene-d8

(3.32%), 4-Bromofluorobenzene

The following data is an example of the precision of representative compounds in the 8260A compound list obtained in the soil mode. The precision was determined on the basis of seven ppb.

Vinyl Chloride (6.82%), (3.52%), Toluene (9.22%), Bromoform
2-Chlorotoluene (4.80%), -Isopropyl Benzene (2.92%), Naphthalene (4.93%).

were also obtained for a five-point calibration covering the concentration range 0.5 ppb-100 ppb. Overall, good precision and linearity can be obtained with the 72. The paper will present complete data for the system in both the water and soil modes.

IMPROVED PHASES FOR THE GC ANALYSIS OF CHLORINATED PESTICIDES

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Despite the fact that many chlorinated pesticides have been banned from routine use in the U.S. since the 1970s, their persistence in the environment still requires routine testing for their presence in drinking and ground waters, soils, waste, and plant and animal tissues. This testing is done at very low ppb levels, requiring careful sample preparation and inert, sensitive analytical systems. Reliable quantitation at low levels depends on adequate separation of individual analytes, low column bleed by ECD detection and the use of analytical column pairs, which permits easy identification and confirmation of individual peaks.

The polymer composition of Rtx®-CLPesticides and Rtx®-CLPesticides2 capillary GC columns were designed and produced using proprietary phase modeling software programs to ensure optimal analyses of the chlorinated pesticides in U.S. EPA Methods CLP and 8081. This study will demonstrate the ability of the improved polymer phases and deactivation method to reduce breakdown of pesticides such as endrin and DDT; which is a common and persistent problem during this analysis. A longer compound list of additional chlorinated analytes (i.e., EPA Method 508 compounds, kelthane, isodrin and all of the common *ortho*- and *para*-isomers of DDT) also were studied to determine if these new columns would provide better separation and confirmation capabilities. Detailed results and chromatograms will be presented.

NEW CONFIRMATIONAL COLUMN FOR THE ANALYSIS OF ORGANOPHOSPHORUS PESTICIDES

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Organophosphorus (OPP) pesticide samples are commonly encountered in environmental laboratories. With the decline of organochlorine pesticides use, OPPs have become the most widely used class of insecticides in the U.S.[1,2]. However, they are not just used for agriculture, but also for termite treatments, lawn and garden sprays, indoor insect sprays and baits, and in pet flea collars and sprays[3]. High-level exposure to these materials may cause acute poisoning. Therefore, testing of groundwater, soils, waste, plant and animal tissues may be required.

GC analysis of OPPs is demanding because some of the compounds are light and temperature sensitive, resulting in degradation, oxidation and isomerization. Specialty detectors (e.g., the nitrogen specific detector or flame photometric detector) and dual-column analysis are used in methods such as U.S. EPA 8141A, in order to obtain low-level detection and identification. Inert injector and column pathways also are essential for good analytical performance. We have designed a primary and confirmational column set for OPP analysis, which features fewer coelutions, decreased analyte degradation and shorter run times than traditional columns. Information will be presented on how the phases were developed using a proprietary phase modeling software program, which directs the optimization of the phase chemistry, film thickness and column dimensions to maximize desired analytical parameters. Data showing the advantages of analysis with this new column pair will be shown.

FAST ANALYSIS OF SEMI-VOLATILE COMPOUNDS FOLLOWING METHOD 8270

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One of the environmental Industries standard tests is EPA SW-846, Method 8270, the analysis of semi-volatile compounds by GC/MS. The target compounds for this method range from low boiling compounds, 2-fluorophenol to high boiling polycyclic aromatic hydrocarbons such as benzo(g,h,i)perylene. There are also many different classes of analytes ranging from polar to nonpolar and include acid, neutral and basic compounds which must be carefully reviewed in order to shorten the analysis time. Due to the complexity of the required target compound list shortening the analysis time of the gas chromatography run has been difficult.

This presentation will show the chromatographic areas of concern to shortening the analysis time and an optimized run for the analysis of method 8270.

MONITORING OF TECHNOGENIC POLLUTION OF AN ENVIRONMENT

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Kazakhstan is rich in mineral resources and with industrial plants, processing them. The ecological situation therefore is dependent on the level of environment pollution. Vital activity and life support are bound to the pollution of water, soil and food.

The majority of provinces was generated around the shafts, dressing plants and ore mining combines. They represent both potential, and substantial hazard to life and health of the populations living there. Therefore, estimation of toxic compounds in an environment as a result of technogenic influence is an urgent problem.

This special concern represents the investigation of an ecological situation in a band of activity of the industrial plants, in particular, gold extracting plants, because of the content of highly-toxic compounds (for example, cyanides, arsenic, heavy metals, etc.) in soil, water, foodstuff, and also in the forages of a vegetative and animal parentage. The hazards of pollution on the territory of industrial plants are conditioned by features of technology envisaging usage of cyanide of sodium; and also from heightened contents of arsenic and heavy metals in an environment due to their availability in processed ores of these components.

The systematic observations of pollution on the territory of an industrial site of one of the plants of Kazakhstan have allowed us to determine the main regularity diffusing of technogenic pollution in an environment of one industrial site and also its nearby agricultural territories and occupied points, as well as its influence on biological plants. On the basis of obtained results of assessment for pollution of this environment it is necessary to develop measures for their elimination.

We established that basic technogenic pollution is diffused from following sources: technological installations, tailings, dumps, the transport of ore and barren rock, and also tailings, within the limits of a sanitary - defensive zone of the plant. Major pollutants are: dust, cyanides and arsenic.

The sampling was carried out many times in different seasons within three years. The monitoring of cyanide pollution reveals the following characteristics: the maximal concentrations of hydrogen cyanide were observed in the atmospheric air at the place of technological process; the results of analysis of cyanide concentration in the snow precipitation confirmed the boundaries of the spreading of hydrogen cyanide in the air; the pollution of surface water by cyanides was observed only during extreme weather conditions. The data from monitoring arsenic have allowed us to determine that the technogenic pollution is added to the natural arsenic in the environment. The plurality of the unfavorable natural factors, bound with a geochemical background of an arsenic, and composition of the soil,

caused heightened amounts of this element in plants on the territory beyond the factory. The pollution of vegetables in limits of a sanitary - defensive zone is explained by usage for irrigation of waste waters of the plant. The maximal level of dust content was observed near the territory of the technological process and along the roads and was two times higher than the limit of permissible concentration. For reduction of pollution in the environment technological recommendations were developed.

The results of ecological monitoring have allowed us to determine basic performances of technogenic of a blooming of pollution from the territory of an industrial site and close lying floor spaces to it. This included the list of the basic toxic components (cyanide compounds, arsenic, dust), level of their concentrations in an environment, distribution on the site. It also allowed to make the estimation of an ecological state of biological plants (plants, fish). Substantiation and assessment of hazard of technogenic pollution by the industrial plants, in particular at gold processing, are thus necessary for improvement of the environment.

EPA XML LABORATORY DATA WORKGROUP - HELP TO USE EXTENSIBLE MARK-UP LANGUAGE (XML) TECHNOLOGY FOR ENHANCING DATA DELIVERY, REPORTING AND PROCESSING UNDER UNIFIED XML STANDARD

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As part of a general interest in better access to environmental information, multiple stakeholders, data users and the public are demanding more data exchange, presentation and reporting of laboratory-generated analytical data. Often this entails customization of data format or arrangement for data exchange. At the same time, shrinking budgets are requiring more cost-effective information management approaches in environmental monitoring, risk assessments, modeling and site assessments. On a parallel track, Extensible markup language (XML) technology is now making a foothold on content and data intensive organizations. Various offices of the Environmental Protection Agency (EPA) have recognized that XML technology with its supporting standards can resolve and help in better environmental data and document management. This technology is web-enabled, format and data independent, and is able to provide a more streamlined, efficient and effective approach to data exchange, search and linked multiple type of data source to render user-oriented formatted reports, forms and presentations.

As part of the EPA's efforts to focus its efforts in the XML arena, The Office of Environmental Information (OEI) organized the XML Technical Assistance Group (XML TAG) to work with different Offices for organizing, developing standards, promoting and demonstrating XML technology to resolve environmental data and document managements' needs. The XML TAG, recognized multiple efforts to develop laboratory analytical data reporting applications occurring across EPA. In response, it organized the XML Laboratory Data Sub Workgroup to provide the following services to environmental community.

1. Establish XML standards for environmental laboratory data and documents for EPA;
2. Promote XML Technology within the laboratory community, Federal and States partners, and stake-holders; and
3. Demonstrate XML application concepts and feasibilities to EPA environmental data and laboratory communities.

The purpose of this paper is to elaborate on EPA's XML Laboratory Data Sub Workgroup goals and how its will work and provide a brief exposure of examples of EPA XML applications. It will summarize plans to work with the laboratory community along with Federal and State partners, and stakeholders in applying XML technology to provide a more streamlined, efficient and effective approach to the exchange, presentation and use of environmental data.

Recommendation

Workgroup to work with the laboratory community along with Federal and State partners, and stakeholders in applying XML technology to provide a more streamlined, efficient and effective approach to the exchange, presentation and use of environmental data.

DEFINITIVE DATA GENERATION FROM AN ON-SITE LABORATORY FACILITY

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In April 1996, the Air Force Center for Environmental Excellence (AFCEE) assumed the lead role in the execution of the Installation Restoration Program at the Massachusetts Military Reservation (MMR) on Cape Cod, Massachusetts.

On-site laboratory services were solicited in 1997 to provide support for a major remedial investigation at MMR. Real time data was required during drilling of groundwater wells to determine the extent of contamination and decide on the placement of the monitoring well screens. The target compounds for the investigation included the following: trichloroethene, tetrachloroethene, 1,1-dichloroethene, *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, 1,1,1-trichloroethane, carbon tetrachloride, BTEX compounds and ethylene dibromide (EDB). Since the reporting limit for EDB is 0.01 mg/L; two separate analyses were required to meet the data quality objectives of the investigation.

The technical specification to the laboratory requested "on-site" analysis for the target volatile organic compounds (VOCs) by GC/MS using method SW846/8260B and EDB with second column confirmation using EPA Method 504.1. Definitive methods were required rather than "screening" type methods for the following reasons: 1) to eliminate the need for ten percent confirmation at an off-site fixed laboratory and 2) to get real time consistent analytical to make immediate decisions.

The On-Site Technologies division of Severn Trent Laboratories was selected to support this investigation. STL established an on-site laboratory consisting of one 45 ft. trailer specifically designed for this project. This facility provides analyses for an average of 25 samples per day. Prior to analysis, the laboratory successfully analyzed an EPA provided PE sample and was audited by both Jacobs and the Quality Assurance Unit of the EPA-New England in Region I.

This presentation will discuss the set-up, operation and management of the on-site laboratory facility, the quality control criteria required for definitive analyses, and the types and numbers of samples that have been analyzed. Comparison data will be presented and recent advances and new methodology will be demonstrated. Program-wide cost savings will also be presented.

RAPID SEDIMENT CHARACTERIZATION (RSC) TOOLS FOR MARINE SEDIMENT ASSESSMENTS

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Rapid sediment characterization (RSC) tools (e.g. X-ray Fluorescence for metals, UV Fluorescence for PAHs, Immunoassay for PCBs and QwikSed bioassay for biological effects) are being used at marine sediment sites to facilitate the ecological risk assessment (ERA) process. However, sites undergoing assessment rarely contain one class of contaminants. Typically, multiple classes of contaminants are present at a site. Therefore, a broad range of screening tools are required to provide a more accurate picture of the contaminant distribution and potential for adverse biological effects as opposed to a single tool. The ability to integrate, interpret and present the RSC results in an effective manner is critical to successfully using these tools to assist with the ERA process. Several commercially available RSC tools have been used together at various marine sediment sites (e.g., NAS Alameda, Hunters Point Shipyard). In order to address the specific goals of each project, different approaches were used for sample analysis, and for the integration, interpretation and presentation of results in a cost- and time-effective manner.

At NAS Alameda, sample analyses were carried out on site. A summation and ranking approach of chemical and biological screening results was used to identify the regions of greatest concern in order to guide sampling for standard regulatory analyses.

At Hunters Point Shipyard, sample analyses were carried out in a fixed laboratory setting. A normalization approach was performed with the chemical screening results to isolate natural from anthropogenic sources of contamination. The chemical screening results were also integrated with historical regulatory results to provide better contaminant distribution maps of the site. These results were used to provide participating agencies with the tools necessary to develop an effective sampling and analysis plan for the Baseline Ecological Risk Assessment. An introduction to the rapid screening tools will be presented along with results from the implementation of these tools at various sites.

ON-SITE INSPECTION OF SUPERFUND PRP MONITORING PROCEDURES

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ABSTRACT

In partnership with the Hazardous Site Cleanup Division (HSCD), the U.S. EPA Office of Analytical Services and Quality Assurance (OASQA) has developed inspection protocols for the review of monitoring procedures being employed by Principal Responsible Parties (PRPs) at Region III Superfund sites. These procedures were evaluated at four Superfund sites (pilot inspections). The purpose of these inspections is to help assure that the monitoring data is of known and necessary quality to support the environmental decisions associated with the sites. The inspections include a review of the sampling and analytical procedures being employed by the PRPs, e.g., long-term on-going monitoring at sites and time critical removal efforts. These inspections verify compliance with site specific sampling and analysis plans. The inspections are being conducted by chemists and emphasize the review of analytical procedures; however, sampling procedures are reviewed, including: documentation; representativeness; containers; preservatives and holding times; sampling equipment (operation and maintenance) and quality control. The review of laboratory operations includes the inspection of: analytical methods and techniques; analytical equipment; quality control; and all associated documentation. The accuracy of the analytical protocols are also verified by providing “blind samples” (true analyte concentrations known to the inspectors but not by the laboratory) called Proficiency Testing (PT) samples. In addition, PRP monitoring data provided to the Agency is cross-checked against actual instrument results and sampling records (“data audit”). The inspection may involve sampling and analysis performed directly by PRP personnel or sampling personnel and commercial laboratory/ies under contract to the PRP. These inspections have been announced and have encouraged partnerships with the PRPs (spirit of working together), as opposed to an atmosphere of “enforcement of policies”. This approach has provided a platform for technical assistance and has helped assure the cooperation of the PRPs and prompt resolution of any findings.

Employing these procedures for the pilot assessments, deficiencies were found with PRP site monitoring, which included errors in sampling, data/record keeping and analytical procedures. In addition, the Quality Assurance Project Plans (QAPPs) for the sites generally benefited from updates, necessitated by the realities of implementation and due to changes in the site clean-up activities. Specific detailed examples of each of these general inspection finding areas will be presented.

The benefits of the PRP on-site assessments have included: reinforcing the importance placed on data quality by EPA to the PRPs, and the public; providing technical assistance to help improve PRP monitoring data quality; assuring effective EPA oversight through additional “field presence”; offering an additional means of information collection for possible “course

adjustments" to site plans to reflect realities of implementation; providing a means to verify actual implementation of site QAPP and Sampling and Analysis Plan (SAP); and afford a check on analytical accuracy (PT samples); as well as providing a check on the level of detail and accuracy of third party reviews.

INTRODUCTION

At the request of the Hazardous Site Cleanup Division (HSCD), OASQA has developed inspection protocols for the review of monitoring procedures being employed by Principal Responsible Parties (PRPs) at Region III Superfund sites. The purpose of the inspection is to help assure that the monitoring data is of known and necessary quality to support the environmental decisions associated with the site. The inspection includes a review of the sampling and analytical procedures being employed by the PRP, e.g., long term on-going monitoring at sites and time critical removal efforts. In addition, PRP monitoring data provided to the Agency is cross-checked against actual instrument results and sampling records ("data audit" [1]).

These inspections serve to provide a means for EPA to maintain a "field presence", verify actual implementation of the site QAPP and SAP and provide technical assistance to the PRPs. The inspections reinforce the importance placed on data quality by EPA to the PRPs and the public.

GENERAL APPROACH

The inspections have been announced and have checked and helped assure compliance with site specific sampling and analysis plans. The inspections have encouraged partnerships with the PRPs (spirit of working together), as opposed to an atmosphere of "enforcement of policies". This approach has provided a platform for technical assistance and has helped assure the cooperation of the PRPs. The sites for the pilots were selected by HSCD and have been explained to PRPs as a new inspection type, which is to be considered "routine" as opposed to targeting poor performance. The pilot inspections have included much input and direction from the site RPMs. This input has been vital to assuring that the inspections met the program and site-specific project goals. Frequent communication with the RPMs will remain a vital part of the SF-PRP inspection procedure in the future. The structure and approach for these inspections that are detailed in this document should provide a basic framework from which any special site needs may be added, e.g., performing unannounced inspections.

SPECIFIC PROCEDURES [2,3,4]

Pre-inspection

* Establish any site specific focus and goals for the inspection from discussions with the site RPM.

* Gather and review background materials including: sampling and analysis plans (SAPs); laboratory quality assurance plans; site safety procedures; PT sample results; data packages and data reviews that have already been performed; results of other inspections (State & EPA); and previously performed QA Project Plan and SAP reviews (the latter via discussions with the OASQA Quality Assurance Team and the RPM).

* Based upon the technical focus of the inspection, establish inspection team membership.

The inspectors are to be knowledgeable in the fields of testing involved and have the necessary inspector credentials and required safety training.

* Notification of PRP: The general time lead for notification via telephone/E-Mail should be a month; however, this may be shortened to a few weeks or days at the direction of the RPMs. The inspection date is to be acceptable to the RPM, the inspection team and the PRP. As activities at SF sites are often complex and involve numerous phases and steps, during the initial communication with the PRP, the team will verify that the file information includes the current sampling plan and analytical quality assurance plans and if not, secure copies from the PRP. In addition, the team must get directions to the site and confirm the safety equipment necessary for the inspection. During these discussions with the PRP, the team is to emphasize the routine nature of the inspection; that it is to assure the quality of the SF monitoring and not an enforcement or adversarial role. The inspection team is to foster a spirit of partnership to help assure the cooperation of the PRP.

* The inspectors will coordinate with the RPM and the PRP to gain access to any off-site commercial laboratories.

* The inspectors will coordinate with the RPM and the PRP to obtain copies of third party independent "data validation" reports.

* Inspectors are to prepare detailed checklists based upon the various site/project sampling, analysis and quality assurance plans. In addition, the inspectors are to collect sampling and analytical method checklists available in the OASQA library and/or prepare such checklists for methodologies not available in the OASQA collection. The methodology checklists should be consistent with the methods cited in the site/project sampling, analysis and quality assurance plans, e.g., "Inorganic On-Site Laboratory Evaluation Checklist"[5], "Organic On-Site Laboratory Evaluation Checklist" for Superfund CLP protocols[6]; 40 CFR Part 136 protocols for NPDES methods[7] and SW-846 for RCRA methods[8].

* The team is to meet at least once prior to the on-site inspection to discuss: the division of team member responsibilities; logistics (directions, contacts, transportation; hotels, etc.); decide on what data (time periods) is to be gathered and reviewed; safety requirements; needed equipment (computers, hard hat, safety glasses and shoes, etc.); and reference materials (checklists, SAPs, QAPs, methods manuals, etc.).

On-site

* The inspection team must carry and present the necessary credentials and complete necessary sign-in and other site-specific entry requirements. The inspection begins with an "Opening Briefing", during which the inspectors explain: the purpose of the inspection; the inspection procedures; the projected schedule (dates and times) for the inspection including personnel to be interviewed; procedures to be observed; data to be gathered and reviewed; the time line and basic topics to be included in the report; a description of "Proficiency Testing (PT) samples; and estimated time for "Closing Conference".

* Inspectors will review PT sample data to assure: the analytical methods and analytes have

been evaluated within the last 6 months with PT/s; the same analytical and QC procedures were employed as for routine SF monitoring; and that the reported results for PTs can be verified by manual re-calculation of the analytical data ("raw data"). The inspectors are to deliver or ship the PRP Proficiency Testing samples for analytes for which the reported results were "Not Acceptable" on previous studies or which the PRP lab has not previously performed analyses in PT studies (within the last 6 months). The team is to inform the PRP that results to these analyses are requested within 30 calendar days and that the results can be exchanged over the phone. If the results for such first time or makeup PTs are "Not Acceptable", the inspectors are to work with the PRP to identify and correct the analytical problem and to then forward additional PTs to confirm acceptable performance.

* Inspectors will: conduct interviews; observe sampling, analysis and quality control procedures being conducted; check analytical equipment; review standard operating procedures; review sample tracking; and associated documentation. In addition, the supporting data for reports sent to the Agency will be tracked from sampling data, chain-of-custody and sample log-in to actual instrument print outs and other unprocessed data ("raw data"), e.g., weighing results for gravimetric results and volumes of solutions for titrimetric analyses, absorbances for spectrophotometric analyses, etc. Inspectors are to employ sampling and analysis checklists as described in the Pre-inspection section of this summary.

* The inspection ends with an exit briefing ("Closing Conference"), at which the findings and recommendations are explained to the PRP managers, and other on-site representatives.

Inspection Reports:

* The reports are to be as brief and to the point as possible (4-10 pages, depending on the number of findings). A short introduction section will include the date and the personnel involved in the inspection. The report will include a listing of the quality control procedures observed at the facility, as well as a listing of analytical methods and instrumentation for each analyte or analysis group. Findings will include: procedures different from those in the site related plans and laboratory QA plan; items shown to adversely affect the quality of the data or completeness of documentation; as well as items contrary to widely accepted good laboratory practices (GLPs). GLP findings will rely heavily upon the experience and judgment of the inspectors. Each finding will reference either specific entries in the SAP or QA Plans, data set, or will indicate "GLP". Also, with each finding will be listed an "Impact", i.e., possible effect of the finding. In some cases, it will be possible to accurately predict the exact impact/s of the finding; in other cases, the indicated impact will be based solely upon the professional judgment and experience of the inspectors. The listed impact should describe the rationale. In addition, each finding is to list a "recommendation", i.e., change in procedures to be consistent with the various site/lab related plans; suggestions to keep the procedures in place and update the plan/s; and suggestions to change the plans and the associated procedures. An example finding from the pilots included: the Laboratory QAP did not address the storage of calibration solutions. The impact: the concentration of the calibration solutions would be expected to decrease with time (these were volatile organic compounds), resulting in the reporting of falsely high sample results, which could result in costly or wasteful decisions. The recommendation: laboratory QAP should address the storage of calibration materials

(conditions and shelf-life), including procedures used to routinely verify the accuracy of stored material, e.g., freshly prepared calibration check standards.

* The report will list the data reviewed ("data audit" portion of the inspection). Also, any problems with the data, records or record keeping system will be included in the "findings" section of the report.

* The report will list the results of PTs already performed by the PRP laboratory/ies within the last 6 months and the results of those PTs the inspection team provided to the PRP for analysis.

* The report will include a "Conclusion" section, in which the overall quality of the monitoring procedures will be summarized.

* The report is to be factual and the opinions of the inspectors on items beyond the scope of this inspection are to be as communications directly with the RPM and not included as part of the report, e.g., suggestions for cost savings in clean-up, etc.

* Reports will be issued initially as "Draft" inspection reports to the RPM and OASQA's QA Team for review and comment. After all comments have been addressed, the "Final Report" will be issued.

* The draft report is to be issued within 30 days of the on-site inspection.

* The final report is sent via registered mail with overnight delivery and includes a cover letter to the PRP requesting a written response to the findings within 30 calendar days of receipt of the report.

Follow-up

* The inspection team is to track the response from the PRP to assure that the requested turn-around-time is met and the team is to call or send a reminder letter to the PRP if the 30 day time frame for written responses or PT analysis is exceeded.

* The RPM is copied on all correspondence to the PRP.

* The inspection team is to contact the RPM and inquire whether the various plans and data provided for the inspection should be returned to the RPM.

* The inspection team is to contact the RPM to assure that the inspection met the RPM's needs and for comments/suggestions for process improvement.

Resources

* The size of the inspection team will be determined by the diversity and complexity of the technical knowledge, skills and abilities needed for the review of the PRP's analytical and sampling procedures. As a minimum, for both safety and technical considerations, two inspectors will be necessary. For the pilot inspections, the teams have included as few as two inspectors and as many as four inspectors. In general, three inspectors will be needed

to perform these inspections.

* Preparation in terms of site plan reviews and laboratory QA plan reviews is a significant portion of these inspections. This also includes various travel and scheduling/logistics considerations. In general, three full days will be needed by the inspection team to review the necessary site specific material and analytical methodologies prior to the on-site inspection.

* The time necessary to perform the on-site portion of these inspections will vary with the monitoring actually being performed. For the pilot inspections, the inspections have taken as little as one day on-site (including travel) to three days not including travel (multiple commercial labs). Based upon the experience gained from the pilot inspections, in general, three full days on-site will be necessary to perform these inspections.

* From the pilot inspections, the time necessary to prepare the inspection report is estimated as two days and includes additional personnel (review by the OASQA Quality Assurance Team). The time for follow-up correspondence, including review of corrective action summaries, and for providing and tracking PT sample results is estimated as two days by one team member.

Inspection Resource Estimates:

Personnel (P)	**Activity**	**Time (T)**	**Resource (P * T)**
3	Pre-Inspection	3 Days	9
3	On-Site	3 Days	9
4	Report Preparation & Review	2 Day	8
1	Follow-Up & PTs	2 Day	2
			Total: 28 Work Days or 224 Hours

SUMMARY

BENEFITS OF THE INSPECTIONS

* Assures the review and validation of sampling and analysis procedures actually being employed by the PRP. This will serve not only as a external, impartial review but may provide information necessary to answer public and other inquiries concerning the quality of the data used for various site related decisions.

* Previously performed reviews of Quality Assurance Project Plans and associated sampling and laboratory quality assurance plans may well be for a different phase of the site work than the on-going monitoring. In those cases, when the Site plans and Lab QAPs have not received review by OASQA's QA Team, the inspection also includes the first review of the

laboratory's QA plans. In cases in which the Site plans and Lab QAPs have received review by OASQA's QA Team, the on-site review verifies that the plans are being fully implemented.

* These inspections provide a detailed review of sampling and analytical procedures (Technical Systems Audit). Such detailed technical review is especially important for analytical procedures, which may include very few quality control checks or which are "method defined", e.g., toxicity characteristic leaching procedure (TCLP). A review of various plans and quality system processes are important but could miss analytical shortcomings in actual implementation.

* Assures an Agency "field presence" and reinforces the message to the PRP and the public that the quality of the data is important to the EPA.

* Provides direct on-site EPA technical assistance to the PRP and/or their contractors. In addition, the inspectors can also provide the PRP with technical contacts throughout the Agency.

* These inspections can help adjust various sampling and analysis plans necessitated by the realities of actual implementation. For example, some items may no longer be relevant or important and should be dropped from the plans, e.g., drop the requirement for a matrix spike duplicate analysis given that a field duplicate is routinely analyzed and is always positive for the target analytes. At one site, analytical procedures and QC were extended over a wide range of target compounds, and a review of data indicated this could be focused on a limited list of materials actually detected on-site. In addition, other items may be found necessary to assure quality and are not in the various plans and need to be added to the protocols, e.g., concern for possible re-contamination of "cleaned waste" at one site. Finally, there may be items in the site sampling, analysis and QA plans which are important, but which have not been included in the actual implementation of the plan, e.g., necessity for the laboratory QAP to address the proper procedure for making corrections to data entry error.

* By confirming that instrument printouts and results can be traced to data previously provided to the Agency (reports to the Agency, collected as part of the pre-inspection activities) not only are the results verified, but the actual sampling, analytical and QC procedures are verified, i.e., not necessarily those procedures included in various plans, and not necessarily procedures indicated through on-site interviews of personnel.

* These inspections include a review of documentation and results from sampling through analysis and data reporting. Regional QA protocols in general require that all data generated for a SF site be validated by an independent third party reviewer. However, significant monitoring at sites may be under Region III State directives, which do not include a requirement for third party review. In addition, some sites pre-date this QA policy and have not received an independent third party review. In these cases, this inspection may provide the first verification of the monitoring results. At sites with independent third party review, this inspection will help follow-up on shortcomings identified by the third party reviewer and help verify the accuracy of the on-going data review.

* These inspections provide PT samples to the PRP's laboratory as additional checks on the accuracy of the analytical procedures.

Status and Next Steps

* Pilot inspections have been conducted at four sites in Region III from October 4, 1999, through March 24, 2000, in Delaware, West Virginia, Virginia and Pennsylvania. The inspection procedures and associated report format were refined as additional pilots were performed. For example, the initial inspection reports did not include potential "impacts" of the findings as were included for later inspections. As indicated in the inspection summary, "impacts" will be included in all future inspection reports.

* At HSCD's request, OASQA is ready to perform additional PRP inspections using the procedures detailed in this report.

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ANALYSIS OF LOW-LEVEL (1ppb - 20ppb) REACTIVE SULFURS IN AIR SAMPLES

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The analysis of reduced sulfur-containing compounds such as H_2S and methyl mercaptan has become more important because of odor complaints near manufacturing sites and refineries. Analysis of reduced sulfur compounds is problematic because of the reactivity of the compounds at low level, ppb range. Because sulfur compounds can react with stainless steel surfaces, Teflon^R coatings or other surface treatments must be used to create a barrier protecting the sulfur compounds from reacting with the metal surface of analytical components. However, there are many problems associated with Teflon^R coating, such as permeability, poor physical characteristics and off gassing.

The Silcosteel^R treatment has been developed which bonds a layer of silica to the inner surface of stainless steel containers, such as high-pressure sample cylinders and ambient air canisters. This coating makes the stainless steel container unreactive to low ppb levels of reactive sulfur compounds. Data and chromatograms will be presented to demonstrate the inertness of the coating on the internal stainless steel surface of ambient air collection containers. The information will contain stability data of reduced sulfurs compounds such as H_2S and methyl mercaptan at 1-20ppb concentrations.

QUALITY, ENVIRONMENTAL HEALTH AND SAFETY IN THE ANALYTICAL LABORATORY

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ABSTRACT

Safety concerns are in many ways similar to quality concerns: "Do it right the first time, every time, safely." The cost of "unsafety" is similar in concept to the cost of "poor quality." There are many other aspects of health and safety programs that parallel the quality system, including policy, procedures, training, tests of proficiency, records of performance, chemical inventory, standards/reagent prep and usage, MSDS, exposure tracking, audits, preventive action, corrective action, root cause analysis, continuous improvement, metrics and problem solving. By recognizing and taking advantage of these similarities in structure, function and operation, a laboratory can integrate its health and safety program with its quality system to achieve better safety and higher quality. An integrated Quality Environmental Health and Safety (QEHS) system helps reinforce desired performance across these common program elements. QEHS integration is an effective risk-based approach to laboratory management. It uses quality tools, applied scientifically and consistently, to continuously improve work processes and products, while protecting employees within a safe work environment.

This paper provides background information, a rationale and a framework for QEHS integration. The elements of a QEHS Management Plan are presented and the responsibilities and authorities of individuals are clearly described. Applicable OSHA regulations are discussed in the context of a Laboratory Chemical Hygiene Plan that is part of the overall QEHS Management Plan. This paper also provides recommendations for successful implementation of a QEHS including communications, information management and record keeping, hazardous waste management and program assessment including OSHA inspections. Assessment strategies are presented, and OSHA inspections are described. Also presented is a summary of safety items to implement with responsibilities identified and guidance on when and how each item should be implemented.

INTRODUCTION

Success and survival in the laboratory field requires effective management of risks while providing accurate, reliable and timely results. Two major risks that must be adequately addressed by laboratory management are safety and environmental compliance. Testing in the laboratory must be performed under safe, accident-free conditions. Samples and hazardous materials, including waste, must be handled in an environmentally sound manner. Lack of compliance with environmental regulations can result in civil and criminal prosecution. An environmental management system (EMS) integrated with the quality, health and safety

program makes good business sense. By identifying the causes of environmental problems, and then eliminating them, an EMS can help save money. More and more often, it is becoming necessary to prove a lab has an EMS to satisfy contract or other business terms.

Many labs have established separate programs to meet legal requirements for health, safety, environmental and quality programs. Quality programs in laboratories are generally well developed to ensure that quality requirements are met. Accredited laboratories must have active quality assurance programs. Health and safety, while just as important to risk management as quality, may not always get the same attention or focus. One way to ensure that health and safety needs are adequately addressed is to integrate them into the laboratory's quality program, to produce an integrated quality, health and safety program.

By recognizing and taking advantage of similarities in structure, function and operation, one system combines these programs in a cost-effective solution that lowers risk and improves productivity and profits. Analytical laboratories benefit from program integration by minimizing or avoiding the costs of duplicate audits, staff and reports. Integration helps reinforce desired performance across common program elements, including training, tests of proficiency, records of performance, chemical inventory, standards/reagent preparation and usage, Material Safety Data Sheets (MSDSs), exposure tracking, audits, preventive action, corrective action, root cause analysis, continuous improvement, metrics and problem solving.

Marilyn R. Block[1] says a comparison of ISO 14001 and ISO 9001 shows only five issues that must be addressed by an EMS are not required by a quality system. These five issues are addressed within health and safety programs.

Legal requirements are identified as part of regular reports submitted by the lab, while *compliance* is evaluated through internal and external audits. Management *communicates* and addresses *emergency preparedness and hazard response* through planning, training, MSDSs, and medical recordkeeping. Emergency drills and scenarios help prepare employees to respond quickly and correctly. *Environmental aspects* of the chemical hazards contained in labs are addressed in procedures for safe handling and waste disposal.

What Health and Safety Requirements Apply to Analytical Laboratories?—Most laws applicable to labs attempt to minimize the likelihood of employee exposure to hazardous chemicals. The Occupational Safety and Health Administration has numerous standards related to this goal. Various Environmental Protection Agency and Department of Transportation regulations also apply, specifying how environmental samples that may contain hazardous chemicals are to be labeled, stored, reported, shipped and disposed. OSHA[2] defines a laboratory as a facility where the "laboratory use of hazardous chemicals" occurs. That is, the handling or use of such chemicals in which all the following conditions are met:

1. Chemical manipulations are carried out on laboratory scale; handling of substances designed to be easily and safely worked with by one person.
2. Multiple chemical procedures or chemicals are used.
3. Procedures are not part of a production process.
4. Protective lab practices and equipment are available and in common use to minimize potential for employee exposure to hazardous chemicals.

Chemicals are defined in several ways, by their characteristics or their effects. Examples include “combustible liquid,” “compressed gas,” “explosive,” “flammable,” “hazardous,” “oxidizer,” “physical hazard,” “reproductive toxins” and “select carcinogen.”

To protect employees from health hazards associated with hazardous chemicals, labs are required to develop and implement a Chemical Hygiene Plan (CHP). It should include SOPs, control measures, use of personal protective equipment (PPE), requirements for fume hoods and other protective equipment, employee training, medical consultation and medical examinations, designation of personnel responsible for CHP implementation, employee information and training, establishment of a designated area for hazardous chemicals, use of containment devices, procedures for safe removal of contaminated wastes and decontamination procedures.

OSHA[3] can provide an interpretation to help evaluate the hazards of chemicals and communicate information to employees. Another OSHA standard[4] is designed to provide employees with information they need to know about the hazards and identities of chemicals they are exposed to while working. The Hazard Communication Standard (HCS) requires information to be prepared and transmitted regarding all hazardous chemicals, covering physical hazards (flammability) and health hazards (irritation, lung damage and cancer). The program requires identifying responsible staff and hazardous chemicals in the workplace, preparing and implementing a Hazard Communication Plan (HCP). The requirements of the rule deal with hazard communication by:

Written hazard communication
Labels and other warnings
MSDSs
Employee information and training

OSHA[5] has excerpted “Prudent Practices for Handling Hazardous Chemicals in Laboratories” published in 1981 by the National Research Council. This is an excellent aid in addressing the elements of an HCP for integration into an overall QEHS Plan.

Who Has What Duties?—In a lab that integrates H&S into its Quality System, the responsibilities and authorities of individuals should be clearly described in a policy document (e.g., the Quality Management Plan). Typically, managers issue policies, provide resources and perform checks in support of the program. Supervisors reinforce the policy and report status. Employees follow the requirements, including recordkeeping and hazard/accident reporting. Assessors verify progress in preventive and corrective actions. Substitute the word “quality” for “chemical hygiene” in the following list and you can see that the duties of the Chemical Hygiene Officer are similar to those of a Quality Manager for training, recording, assessing and improving the program:

- Work with administrators and other employees to develop and implement appropriate chemical hygiene policies and practices
- Monitor procurement, use and disposal of chemicals in the lab
- See that appropriate audits are maintained
- Help project directors develop precautions and adequate facilities
- Know the current legal requirements concerning regulated substances

- Seek ways to improve the chemical hygiene program

How Can a Lab Integrate the H&S Function with Quality?—The following approach is recommended for integration of health and safety with quality:

- Survey and identify types of hazards, work areas and employees possibly affected by current and planned work.
- Map and identify all processes and procedures in the lab that must have safety components included—shipping and receiving, sample storage/prep/disposal, sample analysis, etc.
- Write or rewrite the Quality Management Plan (QMP) and all procedures and processes to include appropriate H&S requirements.
- Provide training on all new procedures and provide hazard communication information.
- Identify areas of commonality that can be put under one line of organization, then assign responsibilities accordingly.

The ten sections of a Quality Management Plan, as described by the EPA[6], can establish a framework for a similar plan to include H&S. This can be used as a QEHS Plan for the analytical laboratory. See Table 1, "QEHS Related Topics."

Communication is the Key to Implementing a Lab Safety Program—Focus on communicating specific details to everyone in the lab, so that QEHS policies and safety procedures will be integrated into the quality system and become part of the overall preventive action program. Train, assess, give feedback, find and fix problems and publicize the solutions. Measure and report progress. Training should include safety awareness, emergency drills, first aid and CPR programs, proper use of safety equipment and appropriate accident response and reporting. Safety equipment training includes personal protection for eyes, face, hand and arm, body protection such as eyewash and shower stations, respiratory gear, face shields and safety glasses, gloves and hoods. Safe practices for handling glassware, reagents, solvents, acids, caustics, gas cylinders and samples with possible carcinogens, explosives or pathogens must be included in the training. Proper labeling and storage must be taught for safe storage, transport and disposal of samples, expired reagents and standards and lab wastes. Use safety meetings, safety themes and drills as opportunities to communicate possible hazards and train employees on appropriate procedures, warning signs and briefings for responding to and addressing:

Toxic, corrosive and flammable chemicals in the lab
Electrical and chemical fires, shock hazards and chemical spills in the lab
At-risk personnel with known allergies, medical conditions, etc. and response

For further guidance, the authors have adapted the "40 Steps to a Safer Lab" by James A. Kaufman, Ph.D.[7]. These steps are presented in Table 2, listing who should be responsible for each step and when.

Information Management and Recordkeeping

Maintaining accurate, up-to-date and easily retrievable records of environmental management activities is essential for reducing future liability (e.g., fines for regulatory non-compliance, costly cleanup costs), facilitating inspections (internal and external) and responding to

customer and other inquiries and information requests. Many environmental laws and regulations require comprehensive documentation to assure compliance and for regulatory agency reporting. Each reporting requirement has unique agencies to work with, reporting periods and submission dates, data reporting formats and record retention times. Documentation requirements are also required to demonstrate conformance with EMS standards such as ISO 14001. Many of these are described in the key environmental management issue subsections provided in Section 3 of the Environmental Management Guide for Small Businesses.[8]

RCRA Hazardous Waste Generator Status

Labs that generate hazardous waste are subject to varying requirements (OSHA, EPCRA) depending on how much hazardous waste they generate and accumulate in a month. To make an initial determination and then track and document the lab hazardous waste generator status from month to month, a facility wide hazardous waste log is recommended. For each waste, record amounts generated and accumulated in the month by waste type, hazardous waste class and characterization method. Also record amounts of all Hazardous Waste and all acutely hazardous waste generated, and accumulated during the month. Once generator status is determined, the lab must develop hazardous waste handling and storage practices and procedures based on all applicable requirements and regulations. Similarly, if a lab meets EPCRA reporting thresholds, it is required to submit a Hazardous Chemical Inventory Form to the LEPC, SERC and the local fire department (40 CFR 370.20). Reference 8 presents an overview of hazardous waste requirements that apply to labs depending on their generator status.

Assessing the QEHS Program— Regularly scheduled, as well as unannounced internal lab audits, can identify unsafe conditions or practices as part of the total assessment. These findings should trigger corrective actions, and the identification of root causes for unsafe conditions and accidents. Metrics should be established, and measurements such as man-hours without accidents, or numbers of incidents by type and impact (lost time, lost dollars) should be recorded. Tracking and trending safety incidents (Pareto analysis) helps quickly identify targets for improvement. These findings may lead to changes in lab facilities and layout, or procedures, the reduction of hazardous reagents through method changes and better inventory management (shelf-life and procurement quality specifications).

What will external assessors (EPA, OSHA) inspect? They will examine documentation of all aspects of the safety and health program to determine if the program elements adequately address hazards at the site and if they meet the OSHA requirements. Examples of documents that may be examined include

- Injury/Illness Logs with supporting documents, such as workers' compensation first reports of injuries, first-aid logs and employee medical records
- Baseline surveys for safety/health hazards, including all industrial hygiene sampling records and MSDS
- Hazard analyses
- Evidence of line accountability—reports of site inspections, accident investigations, documented responses; employee reports of safety and health hazards and suggestions, including documented responses
- Preventive maintenance records

Emergency procedures, including critiques of drills and documented responses
OSHA compliance programs, such as lockout/tag-out, confined spaces and blood-borne pathogens
Training records—training given, curriculum development and review, assessment and documentation
Chemical Procurement—verify proper grades of materials are requested/received, and information on proper handling, storage and disposal is available; inventory and usage records are kept.

Examples of procedures, processes and equipment that may be examined include
Environmental Monitoring—ventilation checks, flow rate of hoods
Sample Receiving and Waste Disposal—handling procedures to avoid personnel exposure and possible sample and/or blank contamination. Includes disposition of excess sample volumes and used containers, outdated chemical reagents and toxic wastes
Maintenance—instrument maintenance and general housekeeping
Personal Protection Equipment—checked for proper function, and to prove it doesn't introduce possible lab contamination if contact with samples occurs
Training—establish that all personnel have received instruction and demonstrated understanding of operating procedures for chemical and equipment handling, emergency responses, reporting, etc.
Chemical Storage—verify gas cylinders are safely secured to prevent falls or heat ruptures and leaks; verify use of safe containers, MSDS, holding conditions and expiration dates of chemicals, neat and in solutions, avoiding personnel exposure and possible sample/blank contamination.

How will assessors conduct their inspections? They may walk through the laboratory and observe work conducted under routine operations for the entire work process, to ensure that the safety and health program is implemented as described in the documents reviewed at the site, and that the program is effective for protecting persons working at the site. They will check known hazard areas for possible problems in work practices, noting hazard categories for appropriate management and any necessary improvements. They will look for evidence that hazards are appropriately controlled, and no others exist, giving special attention to problem areas noted from previous visits. They will conduct informal interviews with randomly selected employees at their workstations regarding work procedures, emergency procedures and personal protective equipment. Formal interviews will be conducted with randomly selected employees in a private setting, addressing work procedures, emergency procedures and personal protective equipment. Managers will be interviewed about the QEHS program and management oversight. At a closing conference or debriefing, the assessors present observations regarding S&H conditions at the site, including hazards found, plans to correct those hazards and program improvements to prevent recurrences of those hazards.

SUMMARY

The broadest application of quality system principles is really risk management. As Greg Hutchins[9] points out, "Risk management is the process of controlling what can go wrong…Only 1/3 of fast growing companies have risk management processes. This results in an opportunity for quality professionals to re-label quality processes and re-deploy quality practices into risk management. And that's the power of quality management. Quality, health,

safety and environmental issues will coalesce into a risk-based approach to management. Continuous improvement, prevention, systems/processes, stakeholder satisfaction, optimum quality for invested dollar, adherence to standards and checks/balances are all quality principles and practices that are immediately transferable to risk management."

When laboratories implement an integrated quality, environmental health and safety program, they not only make their facility a better and safer place to work but they also help to minimize risks that can endanger their future success and increase factors that can improve their success. Employees will be more likely to join and stay with an organization that is concerned for their safety and well being, thereby reducing personnel replacement costs as well as employee injuries. Employees can be more productive if health and safety concerns do not interfere with their work. Clients will be more impressed with laboratories that have a well integrated quality, health and safety program because as well as being able to rely on the laboratory's data they can also have confidence that the laboratory will be around for future business and if previous data is needed for legal purposes. The risks that the client assumes in using a laboratory are greatly reduced if the laboratory's risks are managed. And finally, a laboratory that is focused on risk management as well as quality testing, better serves the industry in which it works, whether it is environmental, petroleum, medical or others, which in the process benefits society and the public interest.

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Table 1. QEHS Related Topics

EPA QMP ELEMENTS	ISO 14001 EMS ELEMENTS	TOPICS TO BE DESCRIBED IN A QEHS QMP
MANAGEMENT AND ORGANIZATION	4.2, Environmental Policy 4.4.1, Structure and Responsibility 4.4.3, Communication	Safety Organization—Organization chart that identifies positions and lines of reporting; authorities and organizational independence of the QEHS Manager and staff and their access to the appropriate levels of management; Lab's process for QEHS dispute resolution; communication routes and policies. Legal requirements (OSHA, EPA, DOT, NIOSH, etc.)—organization's policy on QEHS, including: importance to the organization; general objectives and goals; policy for resource allocation; how management assures the QEHS system is understood and implemented; technical activities/programs supported by QEHS system
QEHS SYSTEM COMPONENTS	All of 4, Environmental Management System Requirements	Roles/responsibilities/authorities of management and staff; system documentation; annual reviews and planning; management assessments; training; systematic planning of projects; project-specific QEHS documentation; assessments; and a list of the tools for implementing each component of the QEHS system. Organizational components supporting the review and approval of procedures for QEHS documentation
PERSONNEL QUALIFICATION AND TRAINING	4.4.2, Training, Awareness and Competence	Policies and processes for: identifying, ensuring and documenting appropriate knowledge, skills, formal qualifications and the need for retraining; safety awareness; emergency drills; SOP preparation, review, approval and use.
PROCUREMENT OF ITEMS AND SERVICES	4.4.6, Operational Control	Processes for reviewing and approving procurement (including suppliers') documents and procured items and services, and ensuring QEHS-related contracting policies are met
DOCUMENTS AND RECORDS	4.4.4, EMS Documentation 4.5.3, Records	Processes, roles/responsibilities/authorities for: identifying QEHS-related documents and records (printed and electronic) requiring control; preparing, reviewing, approving, issuing, using, authenticating and revising documents and records; maintaining documents and records and ensuring legal compliance of records, including transmittal, distribution, retention, access, preservation, traceability, retrieval and disposition;
COMPUTER HARDWARE AND SOFTWARE	4.5.3, Records	Processes for developing, installing, testing, using, maintaining, controlling and documenting computer hardware and software; assessing and documenting the impact of changes; evaluating purchased hardware and software meets requirements; ensuring that data meet applicable requirements and standards.
QEHS PLANNING	4.3.3, Objectives & Targets 4.4.7, Emergency Preparedness & Response	Processes, roles, responsibilities and authorities for: using a systematic planning process, developing, reviewing, approving, implementing and revising the QEHS QMP
IMPLEMENTATION OF WORK PROCESSES	4.4, Implementation and Operation	Development, implementation and management of procedures for: ensuring that work is performed according to approved documents; identification of operations needing procedures; controlling and documenting the release, change and use of procedures; communicating policies, procedures, issues, measurements and decisions

ASSESSMENT AND RESPONSE	4.5, Checking and Corrective Action	Roles/responsibilities/authorities for: Assessing the adequacy of the QEHS system; planning, implementing and documenting assessments and reporting results; picking the best qualified assessment personnel; ensuring that personnel conducting assessments have sufficient authority, management's review and response to findings; identifying how and when corrective actions are taken, ensuring and documenting their effectiveness; dispute resolution
QEHS IMPROVEMENT	4.6, Management Review	Responsibilities for identifying, planning, implementing and evaluating the effectiveness of QEHS improvement activities and ensuring continuous QEHS improvement.

Table 2. Modified 40 Steps to Safer Labs

Step	Company Responsibility	Employee Responsibility	Best Time for Step
1. Policy Statement	Publish and post	Read and understand	Initial Employee Orientation
2. QEHS Committee	Schedule regular meetings	Participate in meetings	Weekly, rotate assignments
3. QEHS Orientation	For new hires; include test on understanding	Pay attention; ask questions; learn requirements; pass test	Initial Employee Orientation
4. Employee health and safety	Promote active involvement	Take care of self and others	Ongoing
5. Employee involvement in safety	Promote safety; assign responsibilities	Follow SOPs; raise issues	Ongoing
6. Safety incentives	Implement and publish	Strive to achieve	Ongoing
7. Safety Manual	Publish and make readily available	Read; follow requirements	Initial Orientation and ongoing
8. Lab inspections	Conduct audits; document findings; monitor responses	Act on nonconformances and prevent potential nonconformances	Regular and unannounced audits and surveillances
9. Safety education	Integrate into work regularly; promote cross-training	Integrate into life; offer lessons learned to others	Courses; ongoing communication
10. Safety meetings	Schedule; provide examples	Participate and contribute	Regular and in other meetings
11. Safety in testing	Discuss at meetings; include safety considerations in SOPs	Read SOPs and MSDSs; apply safety in all tests	Project kickoffs and weekly refreshers
12. Working alone	Prohibit or limit	Don't work alone	Not allowed
13. Unattended test procedures	Prohibit unless proven failsafe; use cutoffs, alarms	Evaluate potential safety hazards of each procedure	Only if essential and can be done safely
14. Hazard awareness	Promote awareness; post signs	Pay attention; know hazards; ask!	Initial orientation and refresher
15. Accidents	Discuss at meetings; promote	Report to management; practice	Stage accidents and

	prevention	prevention	evaluate responses
16. Safety in car and at home	Recommend first aid and CPR training	Apply safety practices, take first aid and CPR training and refreshers	Ongoing
17. Flammable liquids	Limit to minimum amounts; provide dedicated storage area	Check stock and do not over order	Ongoing
18. Smoking, eating and drinking	Prohibit; post signs; provide non-lab eating and drinking area	Don't eat, smoke or drink in lab	Not allowed
19. Food in lab refrigerators	Prohibit; post signs; provide separate refrigerators for food	Put food in designated refrigerator	Not allowed
20. Emergency preparedness for: Fire, explosion, poisoning, spills, vapor release, shock, bleeding, employee contamination	Develop plans; conduct drills; provide training	Participate in drills; learn appropriate responses	Regular training and refreshers. Stage occasional "mock emergency" drill

Table 2. Modified 40 Steps to Safer Labs, Continuesd

Step	Company Responsibility	Employee Responsibility	Best Time for Step
21. Emergency numbers	Post list beside each phone	Know location	Ongoing
22. Segregate acids from bases, and fuels from oxidizers	Store separately as "acid only", "bases only", "fuels only," "oxidizers only"	Know and maintain separate storage	Upon receipt. Return to proper storage after use.
23. Chemical inventory	Maintain up-to-date list	Check stock and do not over-order	Inspect and purge quarterly.
24. Warning signs	Post signs for hazards	Be aware of potential hazards	Ongoing
25. Good housekeeping practices	Provide adequate work and storage space; require good housekeeping	Practice neatness and put "everything in its place"	Ongoing
26. Reduce chemical exposure	Provide adequate work areas, hoods, glove boxes, etc.	Use appropriate work areas and hoods when using chemicals	Ongoing
27. Safety budget	Include in total budget	Advise management of any needs	Annual and as needed
28. Eye protection	Provide eyewear; require use; post signs	Use eye protection when handling samples and chemicals	Ongoing
29. Personal protective equipment, lab coats and gloves, face and benchtop shield	Provide equipment; require use	Use protective equipment when handling samples and chemicals	Employee orientation, ongoing
30. Safety equipment: fire extinguishers, fire blankets, safety	Provide equipment; check regularly	Be aware of location; know how to use	Employee orientation, ongoing

showers and eye wash, first aid kit, fume hoods			
31. Safety documents	Provide central files, maintain current and complete documentation	Know location; read	Annually and as needed
32. Vacuum pumps and gas cylinders	Provide guides for use	Read; use appropriately; ask!	Ongoing
33. First aid equipment	Provide instruction on use; maintain adequate supply	Pay attention; inform management of any needs	Employee orientation, ongoing
34. Electrical connection inside chemical refrigerators	Remove and provide magnetic closures	Comply	Retrofit old or install new units
35. Electrical equipment	Provide grounded plugs on all; install ground fault interrupters (GFIs)	Comply	Retrofit old units, have vendor prepare new units
36. Chemical labeling	Provide labels	Label and only use labeled chemicals	Upon receipt
37. Chemical storage life	Budget for chemicals; provide adequate storage, establish shelf lives	Record date opened; check expiration dates; dispose of expired chemicals	Mark expiration date on label upon receipt
38. Waste disposal	Provide training, implement program	Know requirements; comply	Ongoing
39. Cabinets	Provide fireproof cabinets for storage of flammables	Store solvents properly	Upon receipt; return solvents to storage after use
40. Chemical storage	Provide secure, adequately spaced and well ventilated area	Store chemicals properly; advise management of any problems	Ongoing

PRE-EMPTIVE STEPS THAT CAN MINIMIZE THE COST AND TIME INVOLVED IN DATA VALIDATION

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ABSTRACT

Data validation is often viewed with trepidation. It is necessary to determine data quality and usability but this can often involve a significant investment of time and money. Usually, the requirements for analytical quality control (QC), data validation and data quality objectives (DQO) are determined prior to sample and data collection, and documented in the Quality Assurance Project Plan (QAPP) and/or Sampling and Analysis Plan (SAP). However, when data validation is requested after the fact (often years after the analyses have been completed), major problems can arise. In these cases, limitations in the original data summaries supplied by the laboratories, along with the complications caused by the passage of time can combine to turn even a routine validation project into a time consuming nightmare. Even if independent validation of a data set is not anticipated, there are some "better-safe-than-sorry" steps that can be taken to ensure that any validation required in the future will be relatively pain free. This poster session will address the minimum deliverable requirements, the importance of electronic data deliverables and the validation options that exist when the analytical data package does not support the desired validation level. Minimum requirements and deliverable options are particularly important when working with research laboratories that are not accustomed to compiling data packages for independent validation.

INTRODUCTION

Often, the most difficult data validation projects are those where independent validation was not considered in the original documents (QAPP and/or SAP). For these projects, large amounts of data may have been collected and archived and all is right with the world – until disaster strikes. Maybe regulatory oversight has been transferred to a different agency that is now requiring independent validation before the data can be used; or perhaps an unforeseen litigation is looming in the near future. The saying that "time is money" is especially true when it comes to data validation and the following steps, if taken at the beginning of a project, can greatly reduce the time and money required for unexpected independent data validation.

DELIVERABLE REQUIREMENTS

One of the greatest time-wasters during data validation occurs when adequate data deliverables are not available to the validation chemist. A significant amount of time may be spent combing through stacks of raw data to find information that could have easily been summarized by the laboratory. When preparing the Statement of Work, make sure that the laboratory has the ability to produce a data package that will support data validation. This type of package is routine for most commercial labs; however, many research labs do not have the systems in place to generate more than sample result and associated QC summaries. While a full CLP type deliverable is not necessary, laboratory-generated summaries of surrogates,

internal standards and instrument performance can save time and money during data validation.

Even if the laboratory charges more for this type of data package, it is money well spent. Although most laboratories are capable of generating the necessary summary forms from archived electronic data, and most retain a hard copy of the data for up to five years, it can take weeks for the data to be retrieved from archive and the requested summaries to be completed. When deciding on the type of data package to request from the lab, it may be best to make the assumption that you will not be able to obtain additional deliverables in the future. This will ensure that you have all the necessary information when the time comes for data validation. The various validation levels and the required data package contents are presented in Table 1.

Table 1. Validation Requirements

LEVEL OF DATA REVIEW	QC ELEMENTS	REQUIRED DELIVERABLES
Compliance Screening ***Also referred to as:*** • CCS (EPA) • QA-1 (PSDDA/PSEP) • Cursory • Verification	♦ Holding Times ♦ Method Blank ♦ Accuracy (LCS, MS/MSD, Surrogate) ♦ Precision (MS/MSD, Lab Dup)	♦ Chains of Custody ♦ Sample Result Summaries ♦ Method Blank Summaries ♦ LCS, MS/MSD and Surrogate %R Summaries ♦ Lab Dup, MS/MSD RPD Summaries
Summary Validation ***Also referred to as:*** • Level 3 (EPA CLP) • Level C (Navy) • Screening (AFCEE) • M-2 (organics EPA Region 3) • IM-2 (inorganics EPA Region 3) • CLP summary form review	***Compliance Screening plus:*** ♦ Initial Calibration (ICAL) ♦ Continuing Calibration (CCAL) ♦ Instrument Blanks ♦ Internal Standards ♦ Additional QC (Serial Dilutions, Post Spike Recoveries)	***Screening Summaries plus:*** ♦ ICAL and CCAL Summaries ♦ Instrument Blank Summaries ♦ Internal Standard Summaries ♦ Additional QC Summaries ♦ Raw Data is not required but is highly recommended
Full Validation ***Also referred to as:*** • Levels 4 and 5 (EPA CLP) • Levels D and E (Navy) • QA-2 (PSDDA/PSEP) • Definitive (AFCEE) • M-3 (organics EPA Region 3) • IM-3 (inorganics EPA Region 3)	***Summary Validation plus:*** ♦ Compound Identification ♦ Compound Quantitation ♦ Transcription Checks	***All of the above plus:*** ♦ All Raw Data (this includes all calibration and associated QC samples) ♦ Instrument Run Logs ♦ Sample Prep Logs ♦ Percent Solids Bench Sheets

ELECTRONIC DATA DELIVERABLES (EDD)

Another key factor in streamlining the data validation effort is the availability of electronic data deliverables (EDD). The importance of the EDD cannot be over emphasized; they are especially important when large quantities of data are collected. Through the use of electronic data review software (i.e., EcoChem's Data Quality Screening Tool - DQST©), large volumes of data can be rapidly assessed for the basic QC elements (i.e., precision, accuracy, comparability, detection limits, holding times and bias). These reviews can then be combined with additional manual validation techniques to complete a summary (e.g., EPA Level III) or

full (e.g., EPA Level IV) validation. There are also added benefits to performing this electronic screening, such as the population of a database that that can easily be queried to produce tabulated and graphical representations of the data for site assessment and reporting purposes. A summary of the most basic information required in the EDD is presented in Table 2.

Table 2. EDD Requirements for Use of DQST

Field	Type[1]	Description
Client Sample ID	C	Sample ID as it appears on the Chain of Custody
Sampling Date	D	Date sample was collected
Laboratory ID	C	Laboratory Sample ID
SDG	C	Laboratory SDG or Batch
Analyte	C	Analyte name
Result	N	Final reported concentration
Lab Qualifier	C	Concentration Qualifier (U, J, B)
Units	C	Concentration Units
Reporting Limit	N	Sample Detection Limit or Reporting Limit
Method	C	Analytical Method
Matrix	C	Sample Matrix
Extraction Date	D	Sample Preparation Date
Analysis Date	D	Sample Analysis Date
Dilution Factor	N	Sample Dilution Factor for each analyte
Percent Solids	N	Sample Percent Solids
QCTYPE1	C	Lab QC Identifier (MS, MSD, LCS, DUP)
QCTYPE2	C	Lab QC Identifier (SURR)
QCTYPE3	C	Field QC Identifier (FD, TB, EB, RB)
Spike	N	Spike Added Concentration
Recovery	N	Percent Recovery Value (MS/MSD, LCS, SURR)
RPD	N	Relative Percent Difference Value (MS/MSD, DUP)
Lower Limit	N	Lower %R Control Limit
Upper Limit	N	Upper %R Control Limit
RPD Limit	N	RPD Control Limit

1. Field Type – C- Character, N – Numeric, D- Date
2. Electronic deliverables should contain all results reported on the hard copy of the laboratory report. The file should include all analytical results if they are part of the method being reported, including:
    - Environmental Samples
    - Reference Materials
    - Confirmation Results (for dual columns)
    - Tentatively identified compounds (TICs)
    - Method Blanks
    - Matrix Spikes (MS)/Matrix Spike Duplicates (MSD)
    - Laboratory Control Samples (LCS)
    - Surrogate Spikes
    - Labeled Compounds
    - Re-analyses
    - Field Duplicates/Replicates
    - Dilutions

TIERED DATA VALIDATION APPROACH

So, what can you do if data validation was not included in the project planning process? You already have a project for which data have been collected over a long period of time and you are now faced with the enormous task of having it all validated and, of course, it needs to be done yesterday. You have the EDDs from the laboratory, all of the raw data and basic summary forms, but perhaps not all of the forms required for a full validation. If you proceeded with full validation of all data at this point, it would require a significant investment of time on the part of the data validator to recreate the information from the missing summary forms.

In this situation, a tiered validation approach could save a substantial amount of time and money. First, all data are subjected to an electronic screening using the laboratory EDDs. The results of this screening are compared to the hard copy for accuracy and a certain percentage of the hard-copy data packages are chosen for a full data validation. Packages are chosen based on the results of the screening with emphasis on those that exhibit potential analytical problems. By using this combination of electronic screening to identify potential analytical problems and full validation on a focused subset of the data to determine the source of the problems, the general quality of the laboratory data can be ascertained and any systematic data quality issues identified. The details of the tiered approach are presented in Table 3.

Table 3. Tiered Validation Approach

Validation Level	Information Provided
Compliance Screening (Tier 1) Data Quality Screening Tool (DQST) is used to evaluate electronic data. Qualifiers are assigned to data by the DQST based on control limits provided. An experienced chemist performs a manual review of assigned qualifiers.	DQST Output: • Sample Index • Holding Time Summary • Blank Contamination Summary • Reporting Limit Verification • Blank Spike Recovery Summary • Surrogate Recovery Summary • Matrix Spike/Matrix Spike Duplicate (MS/MSD) Recovery Summary • MS/MSD RPD Summary • Field Duplicate RPD Summary • Laboratory Duplicate RPD Summary • Target Analyte List Verification • Sample Result Summary
Summary or Full Data Validation (Tier 2) In addition to the screening done by the DQST, a manual review of QC elements is performed, based on the desired validation level. The transcription from the hard copy summary forms to the EDD is also verified.	DQST Output (above) plus: • Data package completeness (laboratory documentation for sample receipt, sample analysis and sample result reporting) • Presence and completeness of chain-of-custody documentation • Initial and continuing calibration results • Instrument performance and tuning • Compound identification and quantification – Full Validation only • Review of calculations (from raw data) – Full Validation only • Transcription check (from raw data to final EDD print-out) – Full Validation only

SUMMARY

Investing a little more planning and money up-front, and requesting appropriate deliverables and EDD from the laboratory can realize great savings when independent data validation is required further down the road. The use of a tiered validation approach can allow for a rapid review of all data, with a focus on any data or areas of concern. The use of electronic data screening is indispensable to this effort, and can provide additional benefits due to increased access to and control of the analytical data.

USING CONCRETE CHIPS AS THE MATRIX FOR A PERFORMANCE EVALUATION STUDY

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ABSTRACT

Performance evaluation (PE) samples are submitted to laboratories to assess laboratory proficiency in performing a given analytical method on a specific matrix. PE samples, which are utilized for a variety of regulatory and non-regulatory programs, are typically prepared in deionized water or soil; occasionally, PEs are prepared in oil or air. The promulgation of the new PCB mega-rule, however, has resulted in laboratories being required to analyze concrete chip samples more frequently than ever before. It has, therefore, become increasingly important to understand project laboratory performance relative to the preparation and analysis of concrete chip samples.

Environmental Standards, Inc. recently coordinated and evaluated the results of two PE studies for which customized concrete chip PE samples were prepared and distributed to five project laboratories and to four referee laboratories; one referee laboratory was requested to analyze the PE samples in triplicate. Participation of the referee laboratories in the studies was needed to normalize the data because of the lack of historical data available regarding laboratory performance in the preparation and analysis of a concrete chip matrix. The concrete chip PE samples were analyzed for select polyaromatic hydrocarbons (PAHs), metals and PCBs. The results of the PE studies were utilized by a major gas pipeline company to determine appropriate laboratories to provide analytical services for a concrete remediation project.

The preparative and analytical techniques utilized by the laboratories, as well as the results reported by the five project laboratories and the four referee laboratories for both the single-blind PE study and the double-blind PE study, will be discussed. The statistical trends that were observed relative to the true values and mean referee values will also be presented.

INTRODUCTION

Performance evaluation (PE) samples are test samples that are prepared by spiking known concentrations of specific analytes into a particular matrix. PE samples are typically prepared in either deionized water or soil, but other matrices have also been used. Recently, the analysis of concrete chip project samples has become increasingly more common with the promulgation of the new PCB mega-rule. This rule makes it necessary to determine the extent of contamination throughout the concrete, not just at the surface of the concrete. Consequently, it has become increasingly important to understand laboratory performance relative to the preparation and analysis of this matrix.

PE samples can be either single-blind or double-blind. For single-blind PE samples, the laboratories are informed that they will be receiving a PE sample; however, the laboratories do not know the expected results. In the case of double-blind PE samples, the laboratories being tested are not aware that they are receiving a PE sample. Double-blind samples are typically delivered to a laboratory with other project samples and have fictitious sample names.

Due to concrete being a new PE sample matrix, there is little historical data on PE performance using concrete as a test matrix. To gain information regarding the concrete matrix as a test matrix, referee laboratories are utilized to analyze the PE samples and provide additional independent information relative to the preparative process of the PE samples and to the method applicability to the analytes of interest in the concrete matrix. The PE sample is supplied to the referee laboratories in the exact same way as the sample is provided to the contract laboratories. Performance of project laboratories on the concrete PE samples is then compared to the certified true values of the concentration of analytes in the PE sample and to the mean of the results from referee laboratories during the study evaluation.

Many valuable pieces of information can be obtained from PE sample studies. By comparing the laboratory-reported results to the known certified values, PE samples are utilized both to demonstrate method proficiency and to determine method applicability for the concrete matrix. For example, if all of the laboratories report low recoveries for a particular analyte, there may be a problem with the method for the matrix being tested. If the recoveries of all of the analytes reported by the laboratories are substantially below the acceptance limits, the method is probably not a good fit for the matrix being tested. By comparing the mean referee laboratory results to the project laboratory results, PE studies can identify specific laboratory performance issues and can also demonstrate overall precision among contract laboratories. For instance, if only one of the contract laboratories has extremely low recoveries for the PCB fraction, that particular laboratory may not be completely following all of the procedures as prescribed in the method. Also, because the laboratories are required to provide a full data package deliverable based on the requirements in a project-specific laboratory specifications manual, the PE study gives feedback on laboratory compliance with this specification manual.

PROCEDURE

The six contract laboratories for a natural gas pipeline company that spans nine states took part in two PE studies that utilized concrete as the matrix. The first PE study was double-blind and the second study was single-blind. The same contract laboratories have been utilized for five years for this ongoing gas pipeline investigation. The laboratories have recently been called upon to prepare and analyze an increasing number of concrete samples for PCB delineation; the two PE sample studies were performed to address the need to assess laboratory performance relative to concrete matrix preparation and analysis.

The quality assurance/quality control (QA/QC) oversight contractor initiated the assessment process by contacting a reputable PE provider to custom-prepare the concrete chip PE samples. The PE samples were prepared by spiking the specific analytes into concrete powder and homogenizing the powder completely; water was added to create the concrete. After solidification, the concrete was broken up into concrete chips. The analytes that were

spiked into the concrete were semi-volatiles (specifically, polyaromatic hydrocarbons [PAHs]), PCBs and metals (including mercury). These analytes were spiked into the concrete at levels of three- to five-times the project-required reporting limits as specified in the contract laboratory's specification manual. The organic analytes (*i.e.*, PAHs and PCBs), were spiked into one batch of concrete, and the metals were spiked into a separate batch. The completed PE samples were then transferred into sample jars and labeled with the appropriate analysis test code according to what had been spiked into the sample.

For the double-blind PE study, the PE provider packaged and shipped the PE samples to one of the gas pipeline's field sampling locations where field personnel were collecting investigative samples. The contract laboratories involved in the PE study sent bottleware to the same field sampling location. The field sampling personnel repackaged the PE samples in the laboratory's coolers, made it appear that the PE samples were investigative samples, and shipped the coolers to the contract laboratories. The same batch of customized PE samples was submitted by the PE provider to the four referee laboratories of its choice. One of the referee laboratories performed the analyses in triplicate. The analyses performed by the referee laboratories followed the methods and criteria stipulated in the project-specific laboratory specification manual.

For the single-blind PE study, the laboratories were informed that PE samples were being submitted and consequently, the PE provider simply shipped the samples directly to the contract laboratories.

The contract laboratories prepared and analyzed the samples by SW-846 Method 8270C for PAHs, Method 8082 for PCBs and Series 6000/7000 Methods for metals and mercury. The laboratories submitted their PE results and full data package deliverables to the QA/QC oversight contractor for evaluation. The limits utilized to compare the PE sample results to the true values were similar to project-specific laboratory control sample (LCS) limits typically observed for the analytical methods. For the PAH analysis, recovery acceptance limits of 30-135% were utilized. For the PCB analysis, recovery acceptance limits of 60-130% were utilized. For the metals analysis, recovery acceptance limits of 80-120% were utilized. The limits utilized for comparing the PE sample results to the mean recoveries referee laboratory values were comparable to project-specific matrix spike limits typically observed for the analytical methods. For the PAH fraction, 30-135% were utilized as the recovery acceptance limits. For the PCB fraction, recovery acceptance limits of 50-130% were utilized. For the metals fraction, recovery acceptance limits of 75-125% were utilized.

RESULTS AND DISCUSSION

During the second and fourth quarters of 2000, a double-blind PE study and a single-blind PE study, respectively, were conducted. The results of the double-blind PE study as compared to the true values are reported on Table I and as compared to the mean referee values are reported on Table II. The results of the single-blind PE study as compared to the true values are reported in Table III and as compared to the mean referee values are reported in Table IV.

TABLE I

Analyte	True Value	Units	Laboratory A Recovery	Laboratory B Recovery	Laboratory C Recovery	Laboratory D Recovery	Laboratory E Recovery
Aroclor 1242	147	µg/kg	0%	44.22%	0%	0%	102.04%
anthracene	3,290	µg/kg	0%	26.14%	45.59%	21.28%	0%
benzo(k)fluoranthene	978	µg/kg	0%	14.62%	31.70%	0%	14.56%
benzo(a)pyrene	1,040	µg/kg	0%	14.04%	23.65%	0%	8.82%
chrysene	1,060	µg/kg	0%	31.13%	38.68%	0%	26.04%
fluoranthene	1,670	µg/kg	0%	29.94%	49.70%	23.35%	0%
naphthalene	1,350	µg/kg	0%	0%	25.19%	0%	7.78%
pyrene	2,370	µg/kg	0%	37.55%	59.07%	30.38%	0%
arsenic	1,860	mg/kg	0.32%	0.21%	0.38%	0.22%	0.23%
barium	5,830	mg/kg	16.47%	12.40%	12.68%	14.05%	15.75%
beryllium	7,710	mg/kg	0.01%	0.01%	0.05%	0.01%	0.01%
cadmium	2,430	mg/kg	0.02%	0.02%	0.16%	0.03%	0.04%
chromium	3,330	mg/kg	0.84%	0.74%	0.86%	0.69%	0.77%
lead	4,120	mg/kg	0.39%	0.21%	1.28%	0.23%	0.49%
mercury	356	mg/kg	0%	0.39%	0.15%	0%	0.11%
nickel	2,600	mg/kg	0.46%	0.37%	1.45%	0.42%	0.44%

TABLE II

Analyte	Mean	Units	Laboratory A Recovery	Laboratory B Recovery	Laboratory C Recovery	Laboratory D Recovery	Laboratory E Recovery
Aroclor 1242	105	µg/kg	0%	61.90%	0%	0%	142.86%
anthracene	1,625	µg/kg	0%	52.92%	92.31%	43.08%	0%
benzo(k)fluoranthene	260	µg/kg	0%	55.00%	119.23%	0%	54.77%
benzo(a)pyrene	248	µg/kg	0%	58.87%	99.19%	0%	36.98%
chrysene	560	µg/kg	0%	58.93%	73.21%	0%	49.29%
fluoranthene	808	µg/kg	0%	61.88%	102.72%	48.27%	0%
naphthalene	365	µg/kg	0%	0%	93.15%	0%	28.77%
pyrene	1,525	µg/kg	0%	58.36%	91.80%	47.21%	0%
arsenic	7	mg/kg	83.45%	55.16%	99.01%	56.58%	60.82%
barium	805	mg/kg	119.25%	89.81%	91.80%	101.74%	114.04%
beryllium	3	mg/kg	32.72%	18.38%	128.68%	26.84%	29.41%
cadmium	4	mg/kg	9.80%	12.25%	98.04%	20.34%	24.51%
chromium	28	mg/kg	99.29%	86.88%	101.42%	81.56%	91.13%
lead	60	mg/kg	26.67%	14.67%	88.17%	15.83%	33.83%
mercury	1	mg/kg	0%	190.74%	70.84%	0%	54.50%
nickel	38	mg/kg	31.33%	24.80%	98.69%	28.20%	29.77%

TABLE III

			Laboratory A	Laboratory B	Laboratory C	Laboratory D	Laboratory E	Laboratory F
Analyte	True Value	Units	Recovery	Recovery	Recovery	Recovery	Recovery	Recovery
Aroclor-1242	162	µg/kg	86%	93%	74%	74%	80%	0%
anthracene	3,550	µg/kg	54%	39%	39%	28%	62%	62%
benzo(k)fluoranthene	1,060	µg/kg	35%	0%	0%	0%	35%	59%
benzo(a)pyrene	1,120	µg/kg	0%	0%	0%	0%	30%	47%
chrysene	1,140	µg/kg	57%	39%	32%	30%	65%	82%
fluoranthene	1,800	µg/kg	49%	38%	35%	28%	67%	67%
naphthalene	1,460	µg/kg	27%	23%	34%	0%	42%	41%
pyrene	2,550	µg/kg	82%	47%	43%	37%	75%	82%
arsenic	9.28	mg/kg	138%	106%	91%	103%	112%	127%
barium	1,010	mg/kg	113%	80%	86%	102%	112%	113%
beryllium	4.37	mg/kg	114%	89%	92%	117%	110%	103%
cadmium	5.47	mg/kg	116%	84%	75%	88%	86%	93%
chromium	42.6	mg/kg	114%	90%	91%	100%	112%	106%
lead	70.9	mg/kg	112%	77%	84%	95%	98%	102%
mercury	0.814	mg/kg	110%	118%	135%	100%	100%	0%
nickel	42.7	mg/kg	123%	87%	97%	107%	113%	105%
silver	7.68	mg/kg	203%	100%	65%	92%	96%	26%

TABLE IV

			Laboratory A	Laboratory B	Laboratory C	Laboratory D	Laboratory E	Laboratory F
Analyte	Mean	Units	Recovery	Recovery	Recovery	Recovery	Recovery	Recovery
Aroclor-1242	117.1	µg/kg	120%	128%	102%	102%	111%	0%
anthracene	1,364	µg/kg	139%	103%	103%	73%	161%	161%
benzo(k)fluoranthene	176.2	µg/kg	210%	0%	0%	0%	210%	358%
benzo(a)pyrene	157	µg/kg	0%	0%	0%	0%	217%	338%
chrysene	469	µg/kg	139%	94%	77%	72%	158%	198%
fluoranthene	702	µg/kg	127%	98%	90%	71%	171%	171%
naphthalene	345	µg/kg	116%	99%	145%	0%	180%	174%
pyrene	1,300	µg/kg	162%	92%	85%	73%	146%	162%
arsenic	9.28	mg/kg	138%	106%	91%	103%	112%	127%
barium	926	mg/kg	123%	87%	94%	111%	122%	123%
beryllium	4.28	mg/kg	116%	91%	93%	119%	112%	105%
cadmium	4.61	mg/kg	138%	100%	89%	104%	102%	111%
chromium	35.7	mg/kg	136%	107%	108%	120%	134%	127%
lead	60.1	mg/kg	132%	91%	99%	112%	115%	120%
mercury	0.800	mg/kg	112%	120%	138%	101%	101%	0%
nickel	42.7	mg/kg	123%	87%	97%	107%	113%	105%
silver	5.66	mg/kg	276%	136%	88%	125%	131%	35%

As shown by Table I, the double-blind PE study that was conducted in the second quarter resulted in very low recoveries across the board for all fractions. Table II, indicates that the contract laboratory results were somewhat consistent with the referee laboratory results (*i.e.*, higher percent recoveries when compared to the mean of the referee laboratory results). The analysis of a concrete chip matrix usually results in lower recoveries of spiked analytes than would be expected for most aqueous and soil matrices due to its physical nature and

composition. Therefore, to better gauge the performance of the contract laboratories, it is more meaningful to compare the contract laboratory results to the referee laboratory results as opposed to the true values. One of the project laboratories did not recover any of the PAH or PCB compounds. It was subsequently determined that the incorrect sample jar had been used for the organic tests.

At the conclusion of the double-blind PE study, the project laboratories were given sanitized versions of the PE study results as a mechanism for feedback. The laboratories were requested to identify and investigate their particular problem areas as determined by the PE study and to take measures to correct problem areas. After allowing a couple of months for the laboratories to complete this task, a single-blind PE study using concrete chips was then conducted. As determined by the double-blind PE study, a concrete chip matrix is a little more difficult to analyze than many aqueous and soil matrices. Concrete chip samples have high native concentrations of calcium and consequently sample preparation, including proper homogenization and appropriate clean-up procedures should be followed. For the second PE study, the PE provider supplied the laboratories with detailed instructions for properly preparing and homogenizing the PE sample before analysis. This procedure included grinding the sample into a fine powder to adequately homogenize the sample. For organic analysis, the laboratory was instructed to perform a clean-up of the extract to remove some of the inorganic interference. The laboratories were also instructed to be more careful to utilize the correct sample jar for each analysis. The PE study results on Table III clearly indicate that there was a remarkable improvement in the percent recoveries reported by the contract laboratories as compared to the true values for all analytes. The referee laboratories demonstrated the same improvement (as evident on Table IV). Four of the six contract laboratories did not qualitatively identify all of the PAH compounds in the PE sample, and one of the contract laboratories did not identify the correct PCB. Consistent and improved recoveries were observed for the PCB fraction for all laboratories. Relative inconsistent and variable recoveries were observed for the PAH fraction across the laboratories. The most noticeable improvement was in the metals fraction. Laboratory personnel were more aware of the potential for interference on the project target metal analytes from the high concentration of calcium native to the concrete PE sample.

SUMMARY

The concrete chip matrix is not typically analyzed, and therefore, is not typically used as a matrix for PE studies. Lower recoveries of spiked analytes are typically observed in the concrete matrix relative to the aqueous and soil matrices due to the physical nature and composition of the concrete chip matrix for the sample preparation and analytical methods employed. A double-blind PE study and a single-blind PE study were performed utilizing custom-made concrete chip PE samples. The contract laboratory results were compared to the true values and to the mean referee laboratory values in both PE studies. There was a remarkable improvement in the results of the second PE study that was performed after the PE vendor had supplied the laboratories with specific sample preparation instructions for the concrete chip matrix. The results of the two PE sample studies demonstrate that if the preparation and analysis methods are carefully followed, accurate results can be obtained for the analysis of concrete chip samples. The PE study results also demonstrate good precision and accuracy for PCBs in concrete utilizing the applicable SW-846 methods.

PERFORMANCE-BASED QUALITY ASSURANCE PROGRAM FOR THE ANALYSIS OF PAHS, PCB CONGENERS AND CHLORINATED PESTICIDES IN MARINE TISSUE AND SEDIMENT SAMPLES

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Since the beginning of the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Program in 1987, the National Institute of Standards and Technology (NIST) has coordinated annual intercomparison exercises for the determination of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners and chlorinated pesticides in marine tissue and sediment samples. These intercomparison exercises have become an excellent tool for assessing the comparability of analytical measurements among the marine environmental measurement community. In the 1999 exercise, over 40 laboratories, representing federal and state government, private, and university laboratories, reported results on 18 PCB congeners and 24 chlorinated pesticides in a fresh frozen fish tissue homogenate and on 23 PAHs, 18 PCB congeners and 24 chlorinated pesticides in a frozen marine sediment material. The fresh frozen fish tissue used is candidate SRM 1946, Lake Superior Fish Tissue, while the dry sediment used is candidate SRM 1941b, Organics in Marine Sediment. The laboratories concurrently analyzed reference materials, National Research Council of Canada Carp-I and NIST SRM 1941a, Organics in Marine Sediment. In the 2000 exercise, participants reported results for 26 PAHs, 25 PCB congeners and 25 chlorinated pesticides in a fresh frozen mussel tissue and frozen marine sediment. The laboratories concurrently analyzed NIST SRM 1974a, Organics in Mussel Tissue and SRM 1944, New York/New Jersey Waterway Sediment.

This program operates on a pay-to-participate basis with laboratories receiving a report showing their participation relative to other participating laboratories. A number known only by the laboratory and NIST identifies laboratories. The data from the laboratories are evaluated and combined to assign a consensus value for each analyte of interest in the tissue and marine sediment materials. Z-scores and p-scores are determined for assessment of accuracy and precision. The z-score assesses the difference between the result of the laboratory and the exercise assigned value and can be used to compare performance on different analytes and on different materials. Examples from the reports will be presented.

ORGANIC CALIBRATION RMS IN SUPPORT OF THE EXTERNALIZATION OF EPA'S WATER SUPPLY AND WATER POLLUTION PROFIENCY TESTING PROGRAMS

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As part of the externalization of EPA's Water Supply and Water Pollution Performance Evaluation (PE) studies program, NIST is preparing 20 solution reference materials of a variety of organics in water soluble solvents and 6 solutions of Aroclors in transformer oils. The solutions prepared include two solutions of organochlorine pesticides, many of which are not in existing solution SRMs, two solutions of chlorinated herbicides, a solution of carbamates and vydate, a solution of phthalates and adipate, and two solutions of organic disinfecting by-products. The technical mixtures include toxaphene, chlordane and Aroclor 1016, 1232, 1242, 1248, 1254 and 1260 in methanol along with the same six Aroclors in transformer oils. These 26 solutions will be useful not only to the EPA program but also to companies involved in environmental monitoring, wastewater treatment and other activities.

This presentation will discuss the gravimetric preparation of the solutions, as well as the determination of the purities of the neat chemicals used to prepare the neat solutions. Gas chromatography, liquid chromatography and differential scanning calorimetry have been used for the purity determinations. In all cases, the solutions will be provided in amber ampoules, each containing approximately 1.2 mL of solution with five ampoules per unit. The certified concentrations have been determined by combining the gravimetric data with the concentrations determined from at least one suitable analytical technique, either gas chromatography or liquid chromatography, while taking into account the purity of the neat compounds where applicable. The Certificates of Analysis will provide information on the method of analysis used for confirmation of the gravimetry and the certified values in mass/mass units and mass/volume units, based on a density conversion.

NEGATIVE EFFECTS OF THE "GRAND MEAN" CALIBRATION APPROACH ON GENERATED INTERNAL SURROGATE COMPOUND RECOVERY LIMITS

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ABSTRACT

Several organic calibration implementation options have become available with the promulgation of "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition" (SW-846) Update III; specifically, there are now options for Method 8000B, the method upon which the SW-846 organic analysis methods are based. In previous versions of analysis methods, default (*viz.*, static) limits were provided for the acceptance criteria for surrogate compounds with the recommendation that internally based limits be used when enough data points have been generated to calculate these limits. Such default limits do not appear in current SW-846 method versions, and Method 8000B actually requires each laboratory to generate its own acceptance limits. Method 8000B also provides calibration guidance relative to using the average initial calibration percent relative standard deviations (%RSDs) and the average percent drift or percent difference (%D) for all calibrated compounds to determine the acceptability of initial and continuing calibrations. This acceptance technique is commonly referred to as the "grand mean" approach.

Based on the performance of approximately 100 on-site audits of commercial laboratories in the year 2000 and the third-party validation of thousands of data packages during the same period, the independent laboratory community appears to have embraced the "grand mean" approach when evaluating the acceptance of organic analysis calibrations.

One negative ramification of the "grand mean" approach relates to the generation of laboratory-specific acceptance limits for surrogate compounds. The "grand mean" approach allows the surrogate compound calibration %RSDs and %Ds to vary significantly without any corrective action. Using this approach can easily result in great variability when quantitating surrogate compound concentrations. With two potentially compounding variables (*i.e.*, %RSD and %D), surrogate recovery limits may be significantly wider than the limits based on one variable (*viz.*, "true" recovery). This presentation will provide demonstrations of the negative effects of applying the "grand mean" approach to surrogate recovery limits and will offer evidence to show that a more appropriate approach is to control the variability of the surrogate compound %RSDs and %Ds.

INTRODUCTION

SW-846 methods specify that a laboratory facility must generate surrogate recovery acceptance limits for each analysis performed. The laboratory facility generates the surrogate recovery acceptance limits based on the standard deviation and mean percent recovery of a

minimum of 20 surrogate recoveries from investigative samples. SW-846 methods, however, do not provide surrogate recovery limits to be used as minimum data quality objectives. The laboratory facility is free to apply the surrogate recovery limits generated without controls; therefore, the analytical controls or data quality objectives become very important.

SW-846 methods provide general data quality objectives for the initial calibration procedure. For mass spectroscopy detector (MS) analyses, SW-846 stipulates minimum relative response factors for specific compounds (known as system performance check compounds [SPCCs]) and maximum %RSDs for several specific compounds (known as calibration check compounds [CCCs]). It should be noted that the surrogate compounds are not specified to be SPCCs or CCCs. For MS and non-MS analyses, SW-846 indicates a maximum %RSD for all compounds prior to the implementation of an alternate calibration technique. SW-846 provides two alternate calibration techniques; a curve equation for the compounds that do not meet the maximum %RSD can be generated or the laboratory can use the average of the %RSDs to assess the acceptability of the initial calibration.

SW-846 methods also provide general data quality objectives for the continuing calibration verification procedure. For MS analyses, SW-846 stipulates minimum relative response factors for the SPCCs and maximum %Ds for the CCCs. For MS and non-MS analyses, SW-846 provides a maximum %D for all compounds prior to requiring the instrument to be re-calibrated for the compound(s) that did not meet the acceptance criteria. SW-846, however, allows the laboratory to use the average of the %Ds to assess the acceptability of the continuing calibration verification standard.

The use of the average %RSD or %D to assess the acceptability of the initial calibration or continuing calibration verification standard is commonly referred to as the “grand mean” approach. Based on the performance of laboratory audits and third-party data validation, the vast majority of laboratories has opted to utilize the “grand mean” approach when evaluating initial calibration and continuing calibration verification standards. When using the “grand mean,” the %RSD or %D for the surrogate compounds can be very high and the laboratory is not required to take corrective action provided the “grand mean” is acceptable. This presentation provides examples of how the variability of the initial and continuing calibration can impact surrogate recoveries and the acceptance limits generated from these surrogate recoveries.

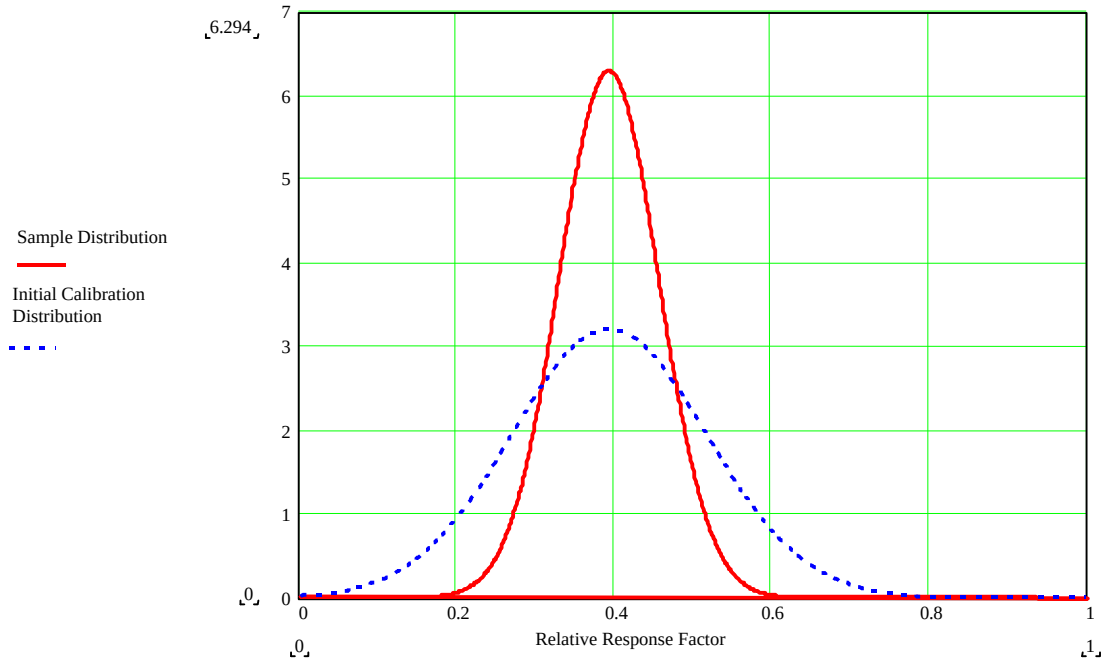
THE “GRAND MEAN” APPROACH FOR CALIBRATIONS

The “grand mean” approach was instituted in SW-846 Method 8000B, Section 7.5.1.2 for initial calibrations and Section 7.7 for continuing calibration verification standards. The approach allows for an initial calibration to be considered valid and usable if the average %RSD of all compounds is less than 15% for MS analyses (provided the CCCs and SPCCs are acceptable) and is less than 20% for non-MS analyses. Situations have been observed during review of laboratory data when most compounds in an initial calibration have a %RSD less than 10% and a few compounds have a very high %RSD; based on the “grand mean” approach, the initial calibration is considered valid because the average of the individual %RSDs is less than 15% for MS analyses or is less than 20% for non-MS analyses. Without specific acceptance criteria for surrogate compounds in an initial calibration, surrogate compounds may be the compounds that display the high %RSDs. Similarly, a continuing

calibration is considered valid and usable if the average %D of all compounds is less than 20% for MS analyses (again, provided the CCCs and SPCCs are acceptable) or is less than 15% for non-MS analyses. Situations have been observed during review of laboratory data when most compounds in a continuing calibration verification standard have a %D less than 10% and a few compounds have a very high %D; based on the "grand mean" approach, the continuing calibration verification standard is considered acceptable because the average of the individual %Ds is less than 20% for MS analyses or is less than 15% for non-MS analyses (even when surrogate compounds display the high %Ds). Surrogate recoveries obtained from an analysis associated with an initial calibration deemed acceptable using the "grand mean" approach might have very high or low recoveries; these very high or low recoveries would affect the laboratory-generated surrogate recovery ranges when the laboratory updates its quality control limits. A similar situation has been observed for continuing calibration verification standards.

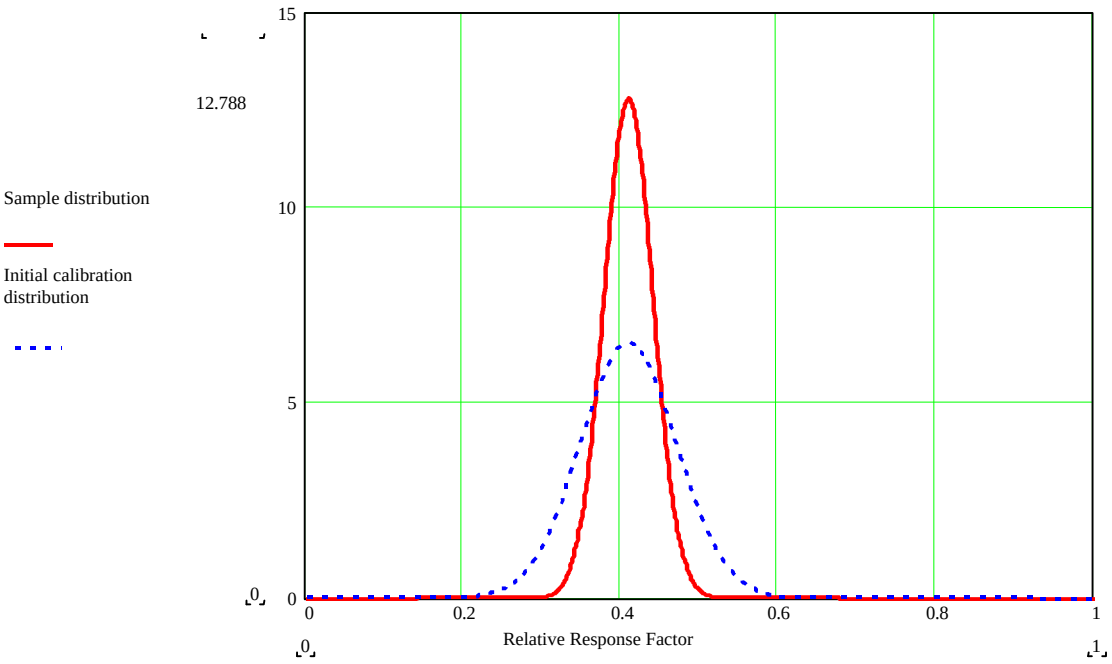
HOW INITIAL CALIBRATIONS AFFECT LABORATORY-GENERATED QUALITY CONTROL (QC) LIMITS

As an example for this presentation, consider the following case that was observed in a laboratory: a 31.6% RSD is observed in the initial calibration for a surrogate compound analyzed by MS analysis. The average relative response factor for the surrogate compound was 0.39313, and the standard deviation of the six relative response factors was 0.124224. For the sake of the example, assume that all analyses for QC samples and investigative samples associated with this initial calibration display results from a Gaussian ("normal") distribution whose average is 0.39313. In addition, assume that 95% of the QC sample and investigative sample results are within one standard deviation (0.124224) of this average (*i.e.*, 95% of all values for the distribution would be within 0.268906 to 0.517354). The resulting Gaussian distribution would have an average of 0.39313 and a standard deviation of 0.0616496. This "correction" of the standard deviation is necessary because it cannot be assumed that multiple analyses of spike standards at one concentration (such as a surrogate compound spiked into QC samples and investigative samples) would have the same distribution as an initial calibration, for which standards of differing concentrations are used to generate the standard deviation and the average. In particular, the standard deviation for the spiked surrogates in the QC samples and investigative samples would be much smaller than the standard deviation from the initial instrument calibration. This "corrected" standard deviation is obtained from the fact that if 95% of the values fell between 0.268906 and 0.517354, the standard deviation for the new distribution would be simply the original standard deviation (from the initial calibration) divided by the *z*-factor corresponding to 95% (two-tailed), or 1.96. The graph below is a plot of both the normal distribution for the response factors obtained in the initial calibration (dashed line) and the normal distribution based on 95% of the sample results being within one standard deviation of the mean (the solid line).

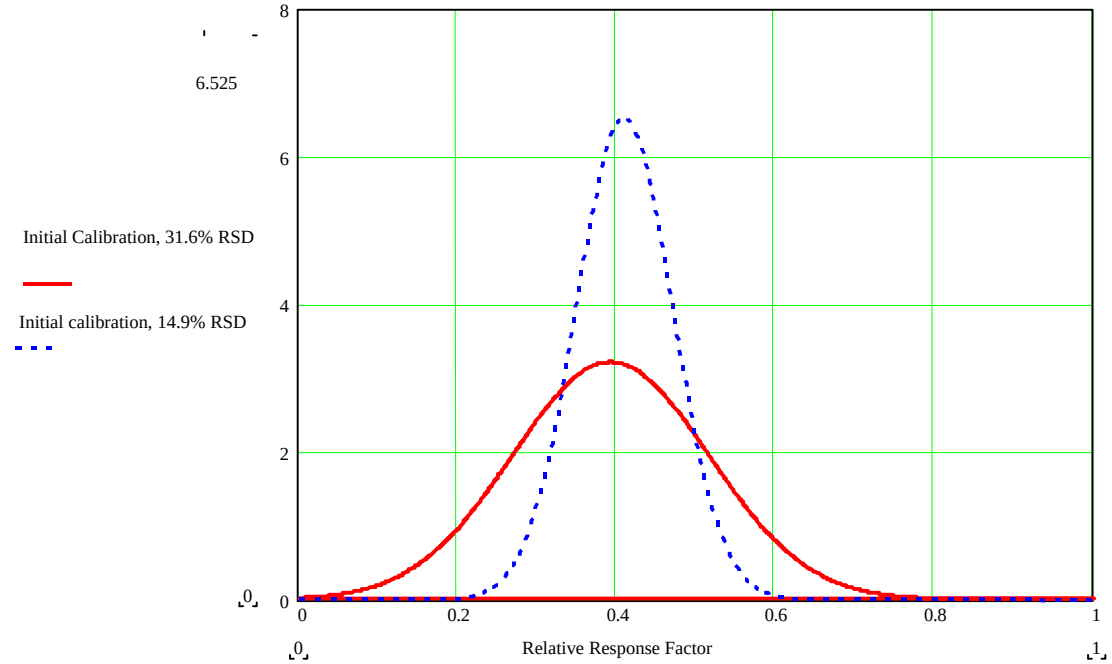


The random number generator in Microsoft Excel was used to generate 50 numbers from this distribution. The 50 numbers represent 50 analyses of QC samples and investigative samples that could be used to develop surrogate recovery limits for the laboratory. Based on the average recovery (calculated as the number from the random generator divided by 0.39313 multiplied by 100%) of 98.3% and the standard deviation of the 50 recoveries (18.8%), the warning limits calculated from the 50 measurements would be 60.8% to 135.8%, and the acceptance limits would be 42.0% to 154.5%.

A similar procedure was followed for an initial calibration that displayed a 14.9% RSD. The average relative response factor was 0.41037 and the standard deviation was 0.061143. The graph below presents the normal distribution for the initial calibration (dashed line) and the distribution used for the random number generator (the solid line). Based on these numbers, the random number generator from Microsoft Excel was used to create 50 random numbers based on a Gaussian distribution with an average of 0.41037 and a standard deviation of 0.0311954 (again, assuming that the sample responses would be within one standard deviation of the mean from the initial calibration). From these 50 numbers, the average recovery was 105.9% and the standard deviation of the recoveries was 7.7%. Based on these numbers, warning limits of 90.5% to 121.2% and acceptance limits of 82.8% to 128.9% were obtained.



An interesting issue to note is the comparisons of the Gaussian distributions from the initial calibrations when the two graphs (from the 14.9% RSD initial calibration and the 31.6% RSD initial calibration) are plotted on the same space. As expected, the plot for the initial calibration with the 14.9% RSD is much more narrow (and therefore would display a better precision) than the plot for the initial calibration with the 31.6% RSD. The graphs are presented below.



HOW CONTINUING CALIBRATION RESULTS AFFECT QC LIMITS

Notice that the above example does not address the continuing calibration verifications

associated with the QC samples and investigative samples. This exclusion is because SW-846 methods for MS analyses require the average relative response factors to be used for the calculation of the sample results for the target compounds and the surrogate compounds and not the relative response factors from the continuing calibration verification standards. But how would a high percent difference in the continuing calibration verification standards affect the quality of the sample results?

For this presentation, we shall use the initial calibration from above where the relative standard deviation is 14.9%, the average relative response factor is 0.41037 and the standard deviation is 0.061143. This scenario yielded a Gaussian distribution for the subsequent QC sample and investigative samples with an average of 0.41037 and a standard deviation of 0.0311954.

Whereas the initial calibration reflected the changes to the standard deviations of the distributions (*i.e.*, the "range" that the results would most likely assume), the continuing calibration verifications display the sensitivity increase or decrease to the instrument (*i.e.*, how the average relative response factor could be affected or how much the average for the distribution shifts). A 30% difference in the direction of decreased instrument sensitivity in a continuing calibration verification corresponds to a value of 0.287259. Assuming the standard deviation has not changed, the Gaussian distribution of results for QC samples and investigative samples would have an average value of 0.287259 and a standard deviation of 0.0311954. The random number generator was used to produce 50 numbers again, and the recoveries of the numbers (calculated as 100-times the number generated divided by the average from the *initial* calibration, since the quantitations are based on the initial calibrations) were tabulated. Every recovery for the numbers generated were less than the 82.8-128.9% recovery limits associated with this initial calibration (created earlier). The recoveries ranged from 55.4% to 79.6%.

A procedure similar to that discussed above was performed, but a 10% difference in the direction of decreased sensitivity was used. This produced a Gaussian distribution for results with an average of 0.36933 and a standard deviation of 0.0311954. The random numbers generated from this distribution displayed recoveries ranging from 73.6% to 103.7%. Ten out of the 50 results were outside of the recovery range of 82.8-128.9%.

For experimental purposes, the same procedures for varying the %Ds were performed in cases when the initial calibration displayed a high percent RSD (>30%). When the initial calibration displayed a high RSD and the continuing calibration displayed a low (10%) difference in the direction of decreased sensitivity, all 50 results passed the rather wide limits generated for the initial calibration (42.0% to 154.5%). The range of recoveries was from 52.0% to 116.8%. When the initial calibration displayed a high RSD and the continuing calibration displayed a high (30%) difference in the direction of decreased sensitivity, two of the 50 results failed the rather wide limits generated for the initial calibration (42.0% to 154.5%). The range of recoveries was from 21.5% to 106.0%. The table below summarizes all of the results for the combinations of RSDs and %Ds. Please note that the numbers were rounded when reported on the tables, and therefore, do not match exactly what was observed in the data set.

	14.9% RSD in the Initial Calibration	31.6% RSD in the Initial Calibration
10% D in the Continuing Calibration Verification	Warning limits = 90.5 - 121.2% Acceptance limits = 82.8 - 128.9% Average of 50 recoveries = 89.4% Minimum recovery = 73.6% Maximum recovery = 103.7% Recovery range = 30.1%	Warning limits = 60.8 - 135.8% Acceptance limits = 42.0 – 154.5% Average of 50 recoveries = 84.2% Minimum recovery = 52.0% Maximum recovery = 116.8% Recovery Range = 64.8%
30% D in the Continuing Calibration Verification	Warning limits = 90.5% to 121.2% Acceptance limits = 82.8% to 128.9% Average of 50 recoveries = 69.1% Minimum recovery = 55.4% Maximum recovery = 79.6% Recovery Range = 24.1%	Warning limits = 60.8 - 135.8% Acceptance limits = 42.0 – 154.5% Average of 50 recoveries = 70.9% Minimum recovery = 21.5% Maximum recovery = 106.0% Recovery Range = 84.5%

SUMMARY

The precision of the initial calibration and continuing calibration verifications indirectly impact the observed surrogate recoveries and subsequently the laboratory-generated control limits for the surrogate compounds. The “grand mean” approach for the initial calibration and continuing calibration verification standard allows the laboratory to utilize poor calibrations for the quantitation of the surrogate compounds. The poor calibrations result in variability in the calculated surrogate recoveries. As the observed surrogate recoveries vary, the laboratory-generated acceptance limits for the surrogate compound recoveries are impacted. The precision of the initial calibration can affect the precision of the surrogate compound recoveries; if the standard deviation is too wide, excessively wide control limits for the surrogate compounds can be generated by the laboratory. Poor accuracy for the continuing calibration verifications can lead to more surrogate compounds failing the quality control criteria. SW-846 does not provide minimum data quality objectives for the surrogate recoveries; therefore, the laboratory utilizes the generated acceptance limits. A high %RSD in an initial calibration can result in laboratory-generated acceptance limits that are very wide (*i.e.*, detected to 200%).

A potential modification to the SW-846 Methods is to add the surrogate compounds to the CCC list, thereby actively controlling the initial calibration and continuing calibration verifications. Another potential modification to the SW846 methods is the presentation of minimum data quality objectives for the surrogate compound recoveries. This modification, however, would impact only the limits that are being used to assess the acceptability of the surrogate compound recoveries. The combination of the two potential modifications would provide increased controls on both the surrogate recovery limits generated by the laboratory and on the overall quality of the data being generated.

REFERENCE

United States Environmental Protection Agency “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition” (SW-846) Update III, December 1996.

AUTOMATED VERIFICATION AND VALIDATION OF CALTRANS STORM WATER ANALYTICAL RESULTS

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ABSTRACT

Laboratory Data Consultants, under a contract with Caltrans Storm Water Management Program through Law Crandall designed and developed a computer application for assessing analytical data presented in an electronic data deliverable (EDD) format. The Caltrans automated data validation application was developed to standardize electronic monitoring data, improves EDD integrity and quality, and provides a cost effective, expedited process to support technical staff in evaluating analytical data. This application, developed within Microsoft Access 97, performs a verification check and automated data validation on a Caltrans-specific formatted EDD. The EDD format uses data fields specified in the Caltrans 2000-2001 Data Reporting Protocols and additional data fields that include quality control batch links and routine accuracy and precision parameters such as surrogate, matrix spike and laboratory control sample recoveries. The application imports an EDD and verifies completeness and conformance with EDD format specifications. Analytical results from related test methods are compared for technical consistency. An error report provides detail for each EDD non-conformance and technical inconsistency. Automated data validation uses a reference project library that contains quality control (QC) and validation criteria specific to the project at hand. The application validates EDDs against these project requirements and a modified version of the EPA Functional Guidelines. Command buttons generate a variety of data validation and QC outlier reports. Database forms also provide on-line review and allow documented editing of data qualifiers, if necessary. A historical assessment report indicates when analytical results fall outside historical ranges. After validation and review, the EDD can be exported either as a text file or Microsoft Excel spreadsheet containing the fields and field order specified in the Caltrans 2000-2001 Data Reporting Protocols.

INTRODUCTION

The Caltrans statewide stormwater monitoring program is an expanding program implemented to assure compliance with regulatory runoff standards. In the past, the program has utilized many laboratories and environmental consultants who may not have necessarily used the same QA/QC and/or data validation standards. This project was initiated to enforce standardization and consistency for the reporting, verification and validation of analytical chemistry data used for stormwater evaluation. Specifically, the goals of this software development project included:

- A standardized EDD format submitted by all Caltrans laboratories;
- Improve integrity and quality of analytical results submitted in EDDs by laboratories;
- Streamline and standardize the data validation process for Caltrans consultants;
- Reduce costs and turn-around-time for review of chemistry results; and
- Produce a standardized data validation output for importing information into the Caltrans database.

Development of this application involved three phases: 1) an EDD file structure to incorporate both the Caltrans data fields and additional information required for an EPA type Level III validation of results reported in the EDD; 2) a comprehensive EDD error checking program to verify completeness and conformance relative to EDD specifications and to ensure that data reported in the EDD are correct and compatible with the validation code and end user's database; and 3) a validation program to evaluate each sample result against associated quality control results, holding times and project-specific validation criteria, and then apply validation qualifiers to those results, as necessary.

The EDD verification or error checker was designed primarily as a laboratory function, while the validation portion of the application was designed exclusively as a tool for the Caltrans consultant. Figure 1 shows the application's main display for the EDD error checker. Figure 2 shows the application's main screen for the EDD validation module.

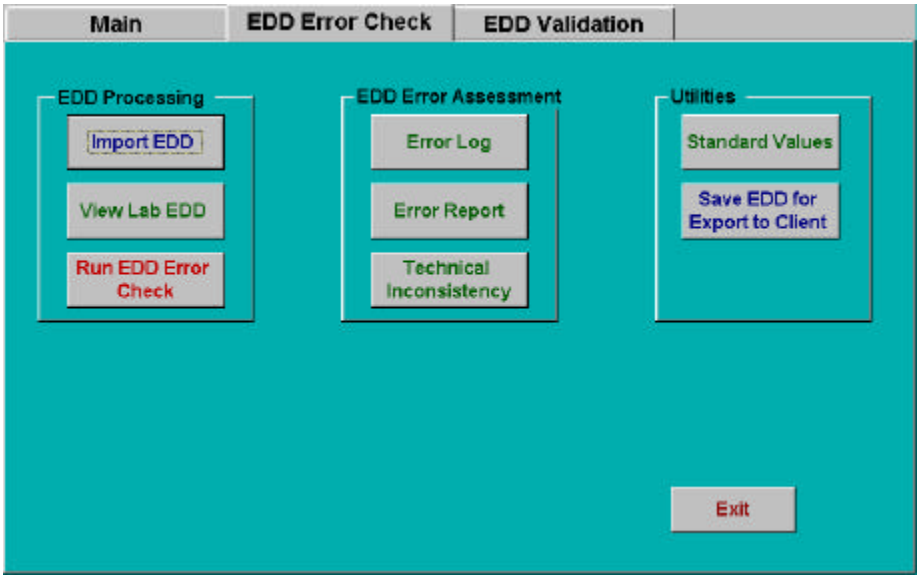

Figure 1. Electronic Data Deliverable (EDD) Checker Main Screen

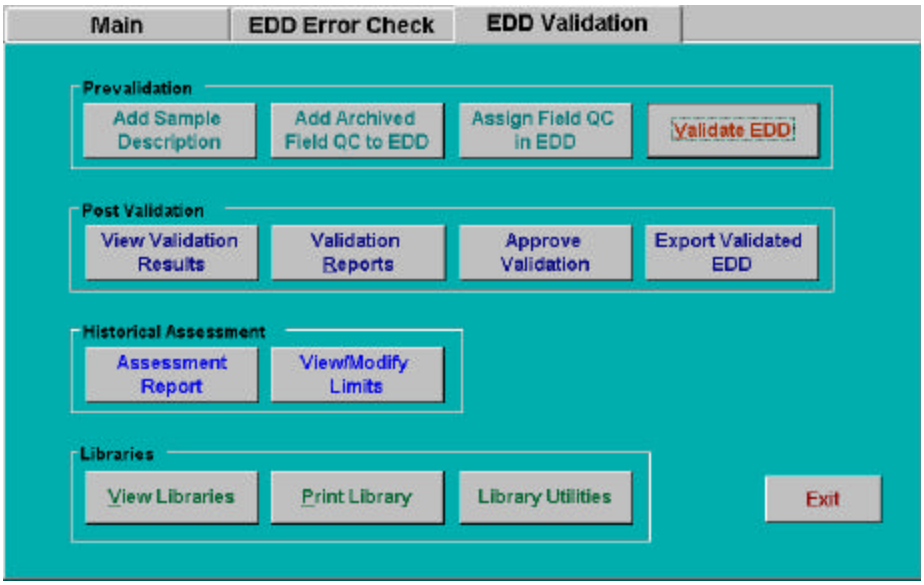

Figure 2. Data Validation Main Screen

ELECTRONIC DATA DELIVERABLE

Two EDD formats exist: one created by the laboratory, which is imported into the application, processed for errors and delivered to the consultant; and the other, which is the exported validated EDD generated by the consultant and delivered to Caltrans. The Laboratory EDD file format incorporates most of the field elements specified in the Caltrans 2000-2001 Data Reporting Protocols, Document No. CTWS-TM-00-001 (June 2000), plus additional fields such as recovery values from laboratory quality control samples, batching links between samples and associated quality control samples and other information used for validation. Table 1 lists the Laboratory EDD file specifications. Laboratories must construct the EDD using the field sequence and specifications listed in Table 1. The application imports either an ASCII, comma-delimited text file or a Microsoft Excel .csv file.

Some sample description fields listed in the Caltrans Data Reporting Protocol (DRP) are not included in Laboratory EDD file specifications (see Table 1) because the chain-of-custody does not provide this information. The consultant appends this information to each EDD after receipt from the lab. A form within the application automates this process. The exported validated EDD includes these additional sample description fields. Validated EDDs exported by the consultant have some information removed from the original laboratory EDD, such as laboratory QC records, and fields used for validation. This information is not relevant to the Caltrans database. The exported validated file contains all the fields in the proper sequence listed in the Caltrans DRP. Two export options allow exporting a validated EDD either as an ASCII, comma-delimited text file or Microsoft Excel spreadsheet file.

EDD VERIFICATION

EDD verification or error checking, which is primarily a laboratory function, serves two purposes: 1) it checks that the EDD is formatted and populated correctly for automated data validation; and 2) it ensures that field values reported in the EDD are compatible with valid values required for the Caltrans Storm Water Management database. With this process occurring in the laboratory, corrections are made prior to EDD submittal. The laboratory

imports the EDD, executes the error checking routine, examines the error report, makes corrections to the EDD if necessary, then exports the EDD and delivers it to the consultant via e-mail or other electronic media.

The verification process examines the EDD for the population of required fields, standard value errors, incorrect date and time formats, logical date and time errors, non-numeric characters in numeric fields, incorrect reporting limits (with dilution correction), missing or duplicate records, related field values inconsistent with each other (i.e., the MDL does not exceed the reporting limit), logical QC batching and missing laboratory quality control records. Errors are written to an error table, which can be viewed on screen or printed as a report. The error report provides detail on each error including the record number and field where each error occurs, if applicable, and a detailed description of the error. Figure 3 shows an example of an error report. The on-screen view also lists each error and error description by record number. A mouse double-click on the record number opens a snapshot view showing all field values for that record along with the error description. The field name and error are highlighted. Figure 4 shows an example of the highlight error table.

EDD Error Detail for Lab Reporting Batch ID: 00-10-0214

Record ID	Field Name	Error Code	Error Detail
	Missing record(s)	0008	Laboratory Control Sample records (where LabSampleType = LCS) are missing for Preparation BatchID 001010a, Method Number 410.4, and Sample Matrix "Water".
	Missing record(s)	0008	Laboratory Control Sample records (where LabSampleType = LCS) are missing for Preparation BatchID 001006a, Method Number 351.3, and Sample Matrix "Water".
	Missing record(s)	0008	Laboratory Control Sample records (where LabSampleType = LCS) are missing for Preparation BatchID 001006a, Method Number 130.2, and Sample Matrix "Water".
	Missing record(s)	0008	Matrix spike records (LabSampleType = MS) are missing in Method Batch ID 001010a for Method Number 410.4 and Sample Matrix "Water".
1	PreparationBatchID	0001	The "PreparationBatchID" field is missing information in this record.
2	PreparationBatchID	0001	The "PreparationBatchID" field is missing information in this record.
3	PreparationBatchID	0001	The "PreparationBatchID" field is missing information in this record.
4	PreparationBatchID	0001	The "PreparationBatchID" field is missing information in this record.
5	MethodBatchID	0001	The "MethodBatchID" field is missing information in this record.
6	MethodBatchID	0001	The "MethodBatchID" field is missing information in this record.
7	MethodBatchID	0001	The "MethodBatchID" field is missing information in this record.
8	MethodBatchID	0001	The "MethodBatchID" field is missing information in this record.
9	MethodBatchID	0001	The "MethodBatchID" field is missing information in this record.

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Figure 3. EDD Error Report

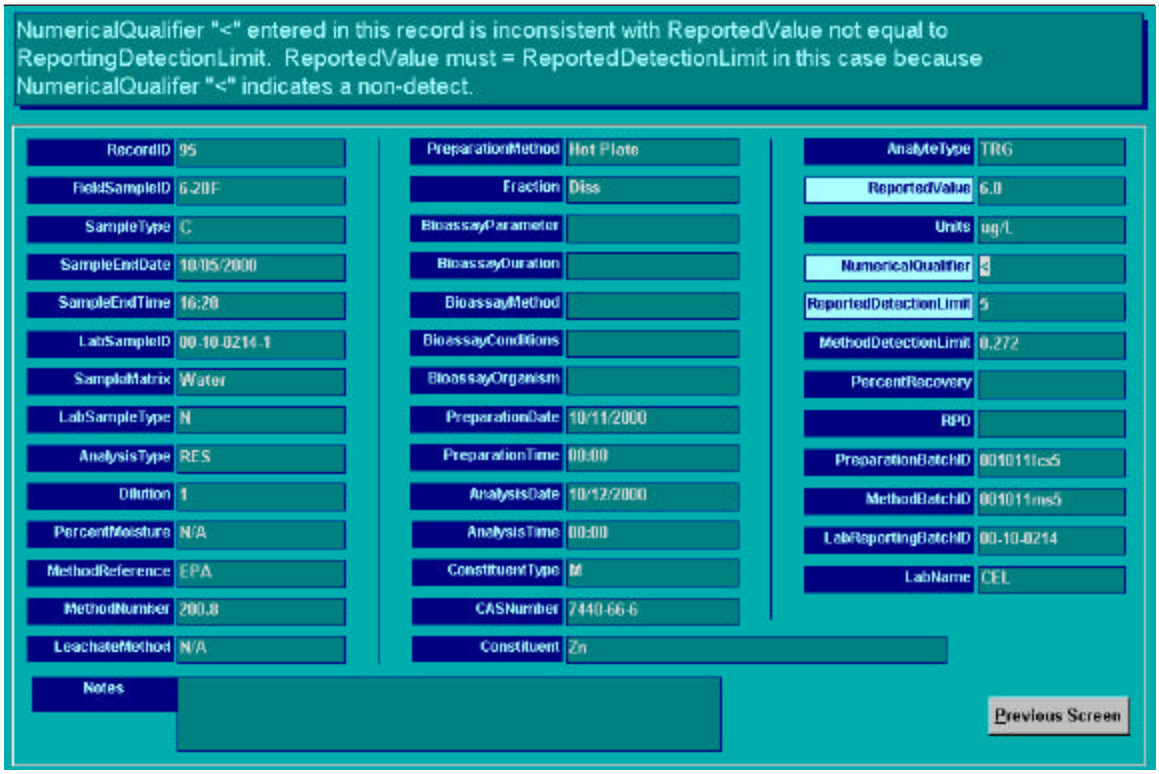


Figure 4. Highlighted Error Table

After correcting any EDD errors, the error checker is run again and the error report reviewed. This process is repeated until all errors have been corrected or any errors remaining are understood and explained. Any corrections made to the EDD must be reflected in the laboratory's Information Management System (LIMS). The EDD is exported as an ASCII text file using a command button utility. This text file is then delivered to the consultant for validation. At this point, the EDD is properly populated including the use of Caltrans standard values.

While the application allows easy retrieval and correction of EDD errors, the user must also make necessary corrections to the laboratory database generating the EDD to ensure hardcopies and EDD match each other.

A separate report details any inconsistencies between related results. These include the following:

- Result reported for a dissolved fraction that is greater than the result reported for a total fraction in a given sample;
- Result reported for hexavalent chromium is greater than the result reported for total chromium in a given sample;
- Result reported for TOC is less the than the result reported for BOD in a given sample;
- Result reported for COD is less than the result reported for BOD in a given sample;
- The ratio between results reported for Total Dissolved Solids and Conductivity is outside the range of 0.52 and 0.78;

- Result reported for TKN is greater than the result reported for total nitrogen in a given sample;
- Result reported for ammonia is greater than the total nitrogen result in a given sample;
- Result reported for TKN is less than the ammonia result for a given sample; and
- pH is outside the range of 1 to13 (inclusive).

Technical inconsistencies present in the EDD do not necessarily require corrective action by the laboratory but they warrant investigation. Refer to Figure 5 for an example of a Technical Inconsistency Report.

Technical Inconsistency Details for Lab Reporting Batch ID: 00-10-0214

Code Number	Technical Inconsistency
0005	The TDS Value of 2 mg/L is too low relative to the EC value of 4 umhos/cm reported for Field Sample ID 8-23C. The ratio of TDS/EC should be between 0.52 and 0.78.
0005	The TDS Value of 4 mg/L is too high relative to the EC value of 3 umhos/cm reported for Field Sample ID 6-20F. The ratio of TDS/EC should be between 0.52 and 0.78.
0005	The TDS Value of 2 mg/L is too low relative to the EC value of 4 umhos/cm reported for Field Sample ID 8-B001. The ratio of TDS/EC should be between 0.52 and 0.78.

Figure 5. Technical Inconsistency Report

EDD VALIDATION

Caltrans' consultants perform automated data validation on EDDs. Refer to Enclosure 1 as a flow chart of the EDD validation process. Each EDD is received from the laboratory as an ASCII or Microsoft Excel.csv text file and imported into the consultant's version of the application. The consultant's version includes both the EDD error checker and the Automated Data Validation Module. Since the laboratory performed an error check on the EDD, a copy of the error report should be submitted along with the EDD. The consultant may confirm the laboratory's error report by running the error checker again.

The first step in the validation process involves populating a number of sample description fields. While automated data validation does not consider this information, it is required for the Caltrans Storm Water Management database, and therefore must be included in the exported validated EDD. A form allows the user to select all or specific samples for updating sample description fields in the EDD. An example of the Sample Description form is shown in Figure 6.

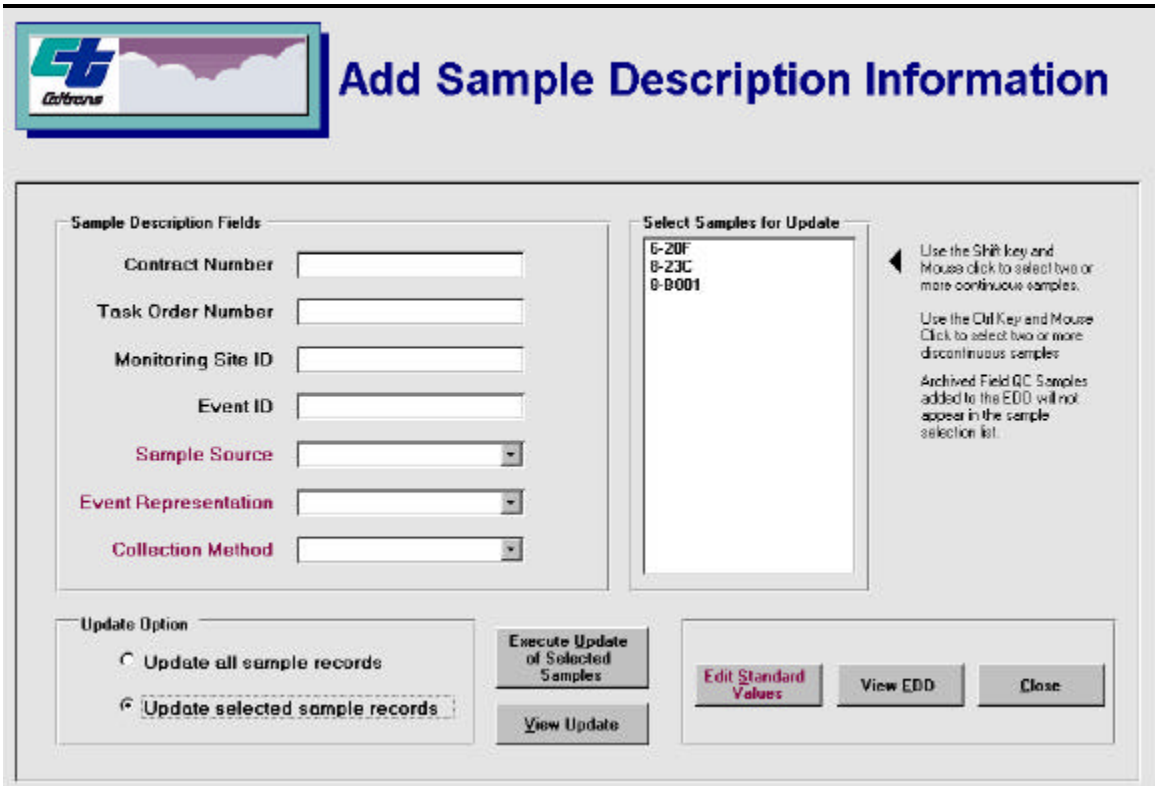


Figure 6. Sample Description Table

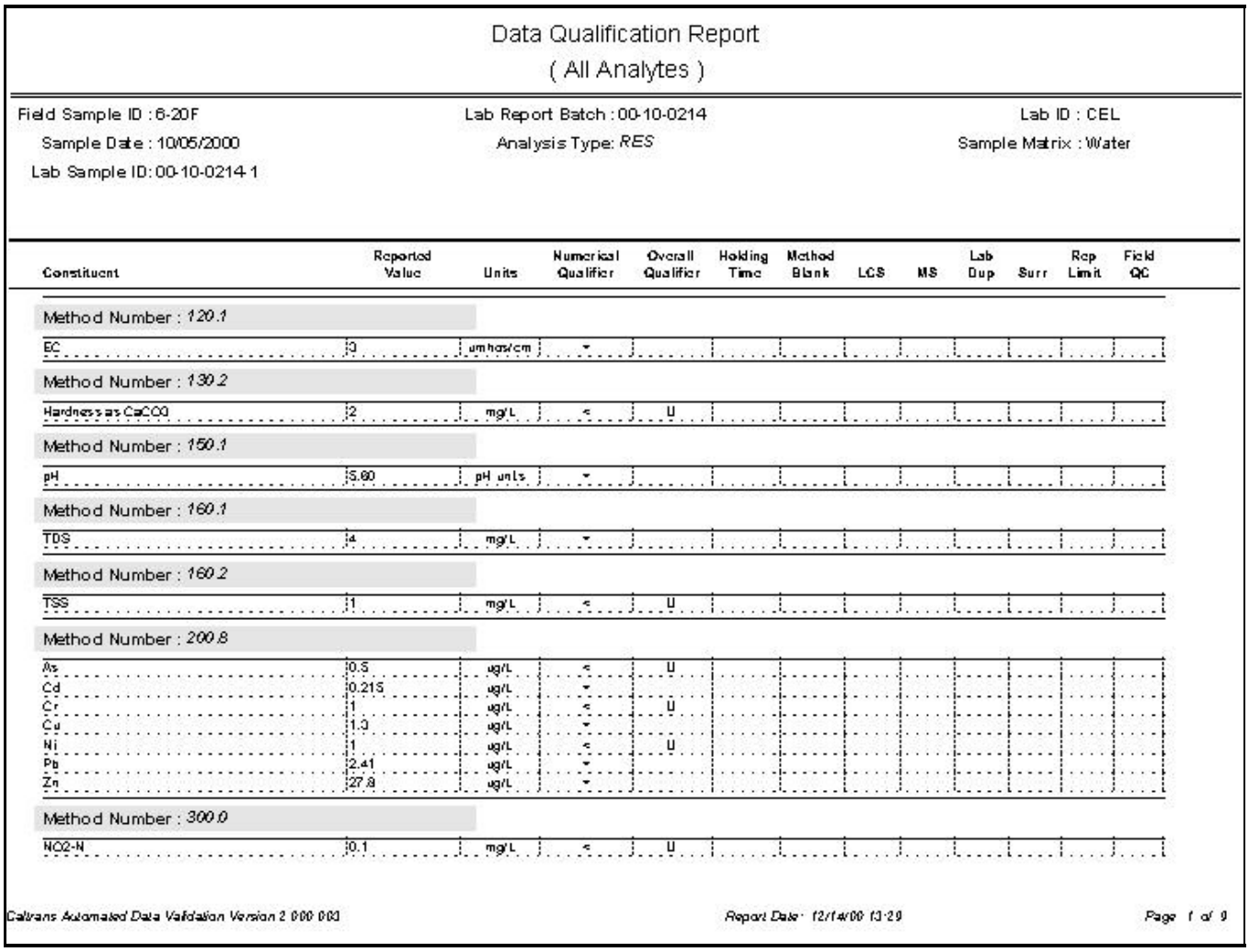
Samples reported in the EDD as field QC samples such as field blanks, trip blanks, equipment blanks or field duplicates must be assigned a field QC type and associated to “true” field samples. Samples identified in the current EDD as field QC samples can be archived, then linked to samples in subsequent EDDs, if necessary. Likewise, any archived field QC samples can be linked to the current EDD.

After making field QC assignments, the EDD is ready for automated validation. A project library is selected, then the automated validation routine is executed. During validation, all laboratory quality control results reported in the EDD are compared against the library criteria. When a quality control result exceeds limits established in the library, a validation flag is appended to the result records in all samples associated to that quality control sample. Holding times are also evaluated from sampling to analysis, sampling to extraction and extraction to analysis dates, whichever apply. Method blanks, field blanks and equipment blanks are evaluated. If target analytes are reported in blanks, appropriate qualifiers are appended to analyte result records for samples associated to these blanks. Validation criteria are provided with the Caltrans library included with the application, but other project libraries can be created with different validation criteria. In this way, the application can validate laboratory data according to a specific project requirement.

REPORTS

The application provides a number of validation summary reports. These include validation reports on a sample basis and Quality Control Outlier reports for each quality control element. The validation reports list sample results by method. Options allow printing all results, all

qualified results or all results qualified as rejected. An example of a Data Qualification report is shown in Figure 7. Quality Control Outlier reports list results for quality control samples that have outliers (values exceeding library criteria). Quality Control outlier reports include a list of all samples and constituents reported in those samples associated to the affected quality control sample. Library validation criteria for the affected constituent are also included in the Quality Control Outlier reports.



Data Qualification Report
(All Analytes)

Field Sample ID : 6-20F | Lab Report Batch : 00-10-0214 | Lab ID : CEL
Sample Date : 10/05/2000 | Analysis Type: *RES* | Sample Matrix : Water
Lab Sample ID: 00-10-0214-1

Constituent	Reported Value	Units	Numerical Qualifier	Overall Qualifier	Holding Time	Method Blank	LCS	MS	Lab Dup	Surr	Rep Limit	Field QC
Method Number : *120.1*												
EC	0	umhos/cm										
Method Number : *130.2*												
Hardness as CaCO3	2	mg/L	<	U								
Method Number : *150.1*												
pH	5.60	pH units										
Method Number : *160.1*												
TDS	4	mg/L										
Method Number : *160.2*												
TSS	1	mg/L	<	U								
Method Number : *200.8*												
As	0.5	ug/L	<	U								
Cd	0.215	ug/L										
Cr	1	ug/L	<	U								
Cu	1.9	ug/L										
Ni	1	ug/L	<	U								
Pb	2.41	ug/L										
Zn	27.8	ug/L										
Method Number : *300.0*												
NO2-N	0.1	mg/L	<	U								

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Figure 7. Data Qualification Report

ASSESSING AND EDITING VALIDATION QUALIFIERS

Validation results can be reviewed on screen. The user can override validation qualifiers using professional judgement when necessary. When an edit occurs, the user is prompted to identify him/herself, the date of change, and reason for change before an update is made to the EDD. Edits to validation flags will not occur if the user fails to document the change.

ADDITIONAL FEATURES

Historical Limits

Sample results reported in the EDD can be compared with the historical range reported for each constituent. This feature is available in the validation module. If a sample result reported

for a particular constituent is above the historical maximum or below the historical minimum for that constituent, the Historical Limit report identifies that field sample ID, constituent, reported value and the minimum or maximum historical value that is exceeded. An example of the Historical Limit report is shown in Figure 8. The table containing historical values can be updated as needed.

Caltrans Storm Water Management Program

Constituent Results Outside Historical Limits

Lab Reporting Batch ID: 00-10-0214

Field Sample ID	Fraction	Constituent	Reported Value	Historical Total Limits Minimum	Historical Total Limits Maximum	Historical Dissolved Limits Minimum	Historical Dissolved Limits Maximum	Units
6-20F		EC	3	10				umhos/cm
		TDS	4	11				mg/L
8-23C		EC	4	10				umhos/cm
		TDS	2	11				mg/L
8-B001		EC	4	10				umhos/cm
		TDS	2	11				mg/L

Figure 8. Historical Limit Table

Project Libraries

As discussed above, automated validation uses a library as its reference when applying validation qualifiers. An example of the library screen is shown in Figure 9.

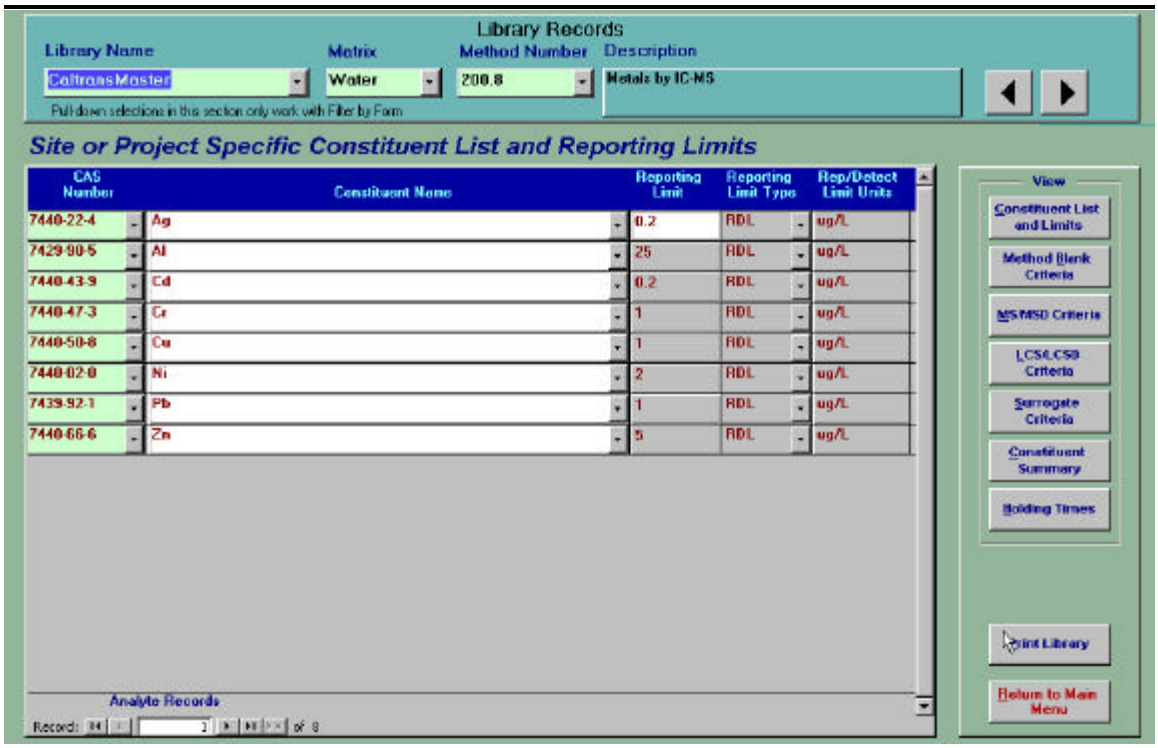

Figure 9. Library Screen

The project library contains the following information:

- All methods identified for use by Caltrans, constituents reported for each method and their reporting limits;
- Lower and upper recovery control limits and RPDs on a constituent basis for laboratory control samples and matrix spikes;
- Blank criteria on a constituent basis (i.e. 5X or 10X rule);
- Method holding time criteria; and
- Rejection point values for each quality control element on a constituent basis. A rejection point is a quality control value or criterion that dictates when a rejected qualifier ("R" validation flag) applies.

Automated data validation uses this information during validation when assessing quality control results and applying validation qualifiers to associated sample results. The application is supplied with a Caltrans master library in its database. By design, the currently released software version does not allow edits to the current library nor does it allow creating a new library. If a new library is needed, the consultant must contact Caltrans data manager. Caltrans data manager can create the new library according to project requirements and submit the new library to the consultant and their laboratories. A utility in both the consultant and laboratory versions allows importation of new libraries. A future version of the application may allow users to both edit and create new project libraries.

CONCLUSIONS

All laboratories and consultants who conduct storm water monitoring are currently using the Caltrans Automated Data Validation computer application. Preliminary assessment indicate that Caltrans Automated Data Validation computer application:

- facilitates the consistent and comprehensive review of the analytical data using project specific guidelines,
- improves the quality of data reported in EDD format since laboratory EDD errors are identified and corrected before submittal to the Caltrans Consultant, and
- is a cost effective tool for evaluating laboratory EDDs.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Caltrans for funding under Contract Number 43A0035, Task Order 1 for this project.

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ADOPTING SYNTHETIC GAMMA SPECTRA FOR QC SOFTWARE VALIDATION

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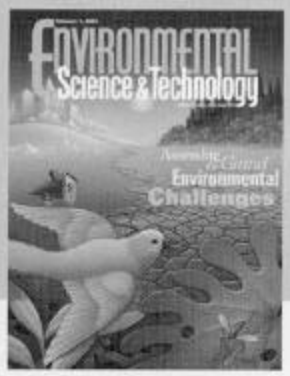
The Department of Energy's Environmental Measurement Laboratory (DOE/EML) located in New York City has, for the past twelve years, been actively involved in supporting the radiation measurement industry as it moves towards a computer based system. A major effort at EML has focused on distributing synthetic radionuclide spectra to evaluate commercially available and "in-house" software package capabilities. These evaluations specifically address accurately identifying and quantifying nuclides in complex gamma-ray spectra. This paper reviews both the overall project status and results of distributing synthetic spectra to the various laboratory participants, and assesses the potential long-term costs and benefits of substituting synthetic spectra for traditional quality control standards and surrogates produced using research reactors and accelerators. In addition, we examine how this technology supports 1) DOE's electronic data validation efforts, 2) DOE's waste avoidance initiatives, 3) DOE's cost control efforts, 4) DOE's health and safety requirements, 5) inventory controls for radioactive standards and solutions and 6) potential for interactions with DOE's long-term stewardship program.

The potential benefits of widespread synthetic spectra technology implementation include: 1) reduced radiological risks, 2) greater flexibility in multiple nuclide selection processes and 3) minimized analytical laboratory radiological sample waste production and associated disposal and infrastructure costs. While the synthetic spectra technology does not totally replace the need for radioactive quality control standards and solutions in the short-term, it does reduce the need to generate selected quality control standards and solutions; and more importantly, improves chemists' ability to accurately and quickly identify and quantify radionuclides in contaminated media. This will, in turn, improve risk assessments and thus allow project and program managers to make better, timelier and more cost effective decisions concerning remediation efforts and long-term monitoring requirements.

AUTHOR INDEX



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