NEW TECHNOLOGIES

INORGANIC ANALYSIS

Reiterating all the factors mentioned, the academia based environmental analytical facilities at present time possess the necessary infrastructure and are ideally positioned as the models for PBMS principles development and application.

USE OF RECORDABLE MEDIA FOR ENVIRONMENTAL ELECTRONIC DATA VALIDATION IN THE PAPERLESS LABORATORY

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The Lockheed Martin Environmental Services Assistance Team (ESAT) at the Region 2 United States Environmental Protection Agency (EPA) assists in the analysis of samples collected from Superfund and Brownfield sites. ESAT provides legally defensible data analyses used for human and environmental assessments. The reporting of the analyses take the final form of "data deliverables" which are cumbersome and difficult to review in their current paper format. In order to facilitate the review and reporting function, a comprehensive system is needed to replace the paper trail with an electronic equivalent. This system would streamline the process without compromising data validity, increase productivity, and minimize issues of error and fraud.

Currently, no definitive standard exists for the creation of such a system although concepts under the Good Laboratory Practices (GLP) program have addressed data validation issues. Computerized systems used to capture, reprocess, report or store raw data electronically must provide for the retention of full audit trails. Any reprocessed data must be traceable to the person(s) by use of timed and dated (electronic) signatures without obscuring the original data. Reasons why any data was reprocessed, e.g., instrument variations, should also be stated.

A method was developed to aid in the reviewing and reporting of the large amounts of data associated with even the smallest of projects. This is made feasible with refined recordable compact disc technology (CD-R) and data processing capabilities at remote computer stations. The data is collected and stored initially on the instrument computer. Upon cursory analyst review, the data and all quality assurance data is transferred to a CD. The data reviewer thus receives a data package consisting of a summary of results, QA/QC summary and index of the raw and supporting data contained on the CD. An autonomous data review software package can simulate the data work up remotely at the data reviewers site enabling efficient and simple review of proper manual integrations, QA criteria, and qualitative and quantitation results.

Once reviewed and validated, the data is transferred for network archival either directly into a Laboratory Information Management System (LIMS) or any other data storage system. In addition, the completed "data deliverable" may be submitted electronically to the client creating a paperless laboratory scheme.

DUPLICATES AND/OR SPLIT SAMPLES ARE OFTEN TAKEN IN ENVIRONMENTAL PROGRAMS

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Duplicates and/or split samples are often taken in environmental monitoring programs and sampling studies. The intended purpose of these data is usually as a check on laboratory performance during a week or other sub period of the entire measuring period. However, it seems that if such samples are actually random samples of an entire monitoring or study period or entire study that such data would provide a valid means of making inferences to the study population concerning the measurement error that existed during the whole period. This information would be useful in the subsequent analysis of the data and for comparisons between studies. An example of a method to

analyze duplicate data using Deming's Method of linear regression, which accounts for error in the x-variable, is presented. The data are Plutonium 239 concentrations in soil. The raw data is used rather than censored data (low values represented as less-than data rather than their actual measured values). We will highlight the advantages of using uncensored data in the analysis of environmental data. The results of the analysis showed that assuming a constant measurement error standard deviation seemed a good approximation to the relationship of error variance to the concentration over most of the range of true concentrations in the study. However, at higher concentrations, there were some indications of increased error variance. The lower detection limit can be defined in various ways, but, in the case of the duplicate samples, this approach yielded lower detection limits in the same ballpark as many of the more conventional methods for determining lower detection limits. Also, the split samples included some spatial variability, and a higher error variance was apparent for this data.

This analysis would have been impossible to do if only censored data were available. This fact and the information derived from this analysis indicates some of the loss of information when data is presented as less-than-detect data.

INTRODUCING A NEW TERM: EFFECTIVE DATA

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Environmental decision-makers and practitioners tend to focus on a dichotomous classification scheme when discussing data. Data is generally seen as belonging to either a Adefinitive Ascreening extreme. In particular, analyses performed on-site (rather than in a traditional laboratory) are often relegated to a Afield screening classification, with the associated assumption that such data have limited application in cleaning up hazardous waste sites. While this may have been true historically, recent advancements in analytical technology are blurring the distinction between Adefinitive and Ascreening. Appropriate exploitation of field analytical technologies, as well as more efficient application of traditional fixed laboratory analyses, will depend on broadening our collective terminology to promote greater professional understanding of how analytical methods are chosen and employed to support environmental decision-making.

The use of a new term, Aeffective data, is here suggested to distinguish data points or data sets that can meet project requirements for supporting decisions without requiring additional confirmatory data to back them up on an individual, data point-by-data point basis. The paper will argue that Aeffective data may allow data generated by screening methods to be used *as if* they were generated by a definitive method *when other conditions are met.* Thus, the term Aeffective data expresses the concept that the information quality of analytical data is not solely dependent on the nature of the analytical method, but also depends upon the associated analytical QC, upon the nature of the decisions that the data are to support, and upon the site-specific context surrounding those decisions.

NEW TECHNOLOGIES

MULTI-MEDIA APPROACH TO SOIL INVESTIGATION OF VOC-CONTAMINATED SITES

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Prior to Update III, VOC losses from conventional soil matrix sampling resulted in data that frequently underestimated the true amount of contamination. In warm dry areas like California and Arizona, state and federal regulators increasingly utilized active soil gas sampling not only for site screening, but also for quantitative characterization of VOCs in soil. With the advent of improved soil preparation methods designed to reduce losses from biodegradation and volatization (EPA Method 5035), the question arises regarding the continued role of soil gas methods for quantitative VOC measurements.

Despite recent improvements, current soil matrix sampling technologies contain inherent limitations resulting in unavoidable VOC losses due to the escape of some vapor fractions. The potential for negative bias is directly proportional to the relative amount of the vapor fraction in a chemical. On the other hand, the in-situ and less disruptive nature of soil gas sampling allows for minimal vapor losses, making it well- suited for measuring this most elusive phase. However, using vapor phase measurement to calculate total VOC concentration is an indirect method that relies on phase partitioning assumptions and the use of site-specific soil and chemical parameters.

This paper proposes a multi-media approach to site characterization, based on a recognition of the inherent advantages and limitations of both soil matrix and soil gas sampling methods. The soil gas method is conducive for chemicals with a high vapor fraction, while soil matrix method favors chemicals with low vapor fraction. The vapor fraction of a chemical can be easily estimated based on three-phase partitioning assumptions and the use of appropriate soil and chemical parameters. Understanding the vapor fractionation characteristic of each chemical of concern should be the starting point of any site investigation and the basis for an effective multi-media strategy.

However, having two sets of data (which may not always agree) is a significant departure from previous practice and introduces complications for project managers and regulators who use the data to make risk management decisions. This is an unavoidable consequence of this approach, and it places a greater burden on the investigator to constrain the reliability and accuracy of each type the data. This also underscores the reality that while the state of science with both soil matrix and soil gas technology has greatly improved our ability to measure VOCs in soil, there is no “one-method-fits-all” and that both methods are imperfect tools for approximating the true amount of VOCs. On the other hand, the alternative of relying on only one type of data, despite the recognition that different VOC species can behave differently, is far less acceptable from the perspective of protecting human health and the environment.

UPDATING WASTE SITE PRACTICES

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EPA is coordinating the development of support mechanisms to encourage modernization of hazardous waste site characterization and cleanup practices. The Agency believes that modernization will enable the haz waste industry to more efficiently adopt innovative technologies and strategies that can speed site cleanups while maintaining or improving the protectiveness and cost-effectiveness of site activities and desicions. A paradigm that has been demonstrated to accomplish that goal is an integrated triad of systematic planning, dynamic work plans, and on-site measurement technologies. Coordinating the upgrading of a regulation-driven industry is a daunting challenge. TIO plans to use a variety of outreach mechanisms:

- Internet seminars
- case studies,
- Clu_in,
- Tech Direct,

to increase the awareness of

- state agencies and organizations (ITRC, NEWMOA),
- consumers of these services (such as PRPs, bankers, real estate brokers, insurance brokers),
- policy makers.

ONSITE ANALYSIS – COST EFFECTIVE AND FAST: CASE STUDIES

I. Rhodes

Site investigations usually involve the collection of soil borings and the installation of groundwater monitoring wells following a previously defined plan. Samples are sent to an offsite laboratory which may take weeks to report the results. The results are typically reviewed by an engineering consultant who, upon data review, may realize that another plan must be developed and executed to better delineate the extent of contamination and to assess potential receptors. Multiple parties may review/approve several plans. Several iterations may be necessary to properly assess the site. The same approach may need to be followed during site remediation. Field analytical methods facilitate the process because they provide real time accurate results to allow collection and analysis of relatively large number of samples cost effectively. This capability results in a better definition of nature and extent of contamination and allows for quick on the spot decision making as new knowledge is acquired. In addition, a complete investigation and even closure can be done in days, samples to offsite labs for confirmation are minimized, and it may not be necessary to repeat mobilization of drilling equipment. Any needed permanent wells can be appropriately placed and the information gathered can be used to input remediation plans.

This presentation includes results of the field use of simple techniques such as colorimetric strips to measure nitrate in groundwater, immunoassay kits for the determination of PCBs in soil, as well as on-site use of more complex instrumentation like GC and GC/MS. In all cases, the project time was reduced by at least a factor of five with significant cost savings of at least one third.

THE BUSINESS OF MAKING A LAB FIELD-PORTABLE

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Abstract: With the wide range of field-portable instrumentation now available, it is possible to perform rapid, high quality analyses at the site of investigation. In fact, this approach is quickly becoming more accepted and even required. People who use field-portable equipment quickly realize (often the hard way) that there is a lot more to doing analyses in the field than owning a cool instrument. This paper will discuss the challenges, concerns, strategies, and success of life in the field.

EXPEDITED SITE CHARACTERIZATION AND REMEDIATION: AN INTEGRATED APPROACH TO SAVE TIME, MONEY, AND HEADACHES

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Abstract
The Wenatchee Tree Fruit Research and Extension Center, located in Wenatchee, Washington, included a former U.S. Public Health Service/EPA pesticide test plot area and a laboratory drain field, in addition to an active university research facility. As a result of chlorinated pesticide disposal experiments, a test plot area was contaminated at levels of concern. EPA asked the Corps of Engineers to design and implement the characterization and remediation activities.

The Corps, after reviewing existing site data, proposed on-site analyses using immunoassay analysis (IAA) kits for chlorinated pesticides combined with a limited amount (~ 10%) of fixed laboratory data. The fixed laboratory results included organochlorine, organophosphorus, carbamate and paraquat-based pesticides. This approach would result in a more efficient characterization of the Test Plot than only fixed laboratory data. The Corps also believed that this approach would make it possible to segregate soil into various waste streams shortly after excavation, allowing for better disposal options. EPA, the State of Washington Department of Ecology, and Washington State University (the landowner) agreed with using this approach and assisted the Corps with removal action planning and completing the investigation.

The Corps implemented an integrated site characterization and remediation, allowing for characterization and immediate excavation and segregation of soil. A pilot test using contaminated surface soil from the site provided initial action levels for the DDT and cyclodiene IAA kits. On-site analysis action levels were refined during the characterization using fixed laboratory confirmation results. This was necessary because the Corps believed the relative proportion of cross-reactive compounds varied with depth and location. On-site analytical results were available within hours of sample collection. Soil excavation was planned in the field, using the analytical results with a Corps-developed decision matrix. Garry Struthers Associates, the Corps' investigation and removal contractor, completed the project work in conjunction with the Corps. The project was successful. The Test Plot no longer contains soils exceeding the site action levels.

This paper presents the development of the field analytical strategy and the decision tree that was developed to make sure that the final disposition of the impacted soil met both the federal and State of Washington waste designation criteria and state soil cleanup criteria (Model Toxic Control Act). The spreadsheet-based tools for handling the immunoassay logarithmic calibrations and the presentation of the three-dimensional excavation plan will be described. The ease and issues arising from use of on-site laboratory results and fixed laboratory sample results, as well as lessons learned, will be addressed in the presentation.

Introduction

The Tree Fruit Research and Extension Center (WTFREC), located in Wenatchee, Washington, includes a former U.S. Public Health Service/EPA pesticide test-plot area and a laboratory drain field, in addition to an active university tree fruit research and extension center. As a result of chlorinated pesticide weathering experiments, the test plot of approximate dimensions 90 feet by 35 feet had been contaminated with DDT, DDE, DDD, Endosulfan I, Endosulfan II, endrin, dieldrin, lindane, and parathion above known levels of concern for human health and the environment. The US Environmental Protection Agency (EPA), Washington State University (the current property owner), and Washington Department of Ecology determined that remediation of the test plot area was necessary. The EPA requested the U.S. Army Corps of Engineers - Seattle District to propose, design, and implement the characterization and remediation.

Excavation was selected as the remedial approach in order to meet a variety of considerations. The pesticides had

been mixed with a variety of chemicals, such as lime, and placed in discrete locations at the surface and at a depth of two to three feet in the plot. Based on the experimental results and investigation data from EPA and Washington State University (WSU), it was believed the contaminants had not migrated more than several feet away from their initial locations in the test plot. Thorough characterization was needed to determine which areas of soil would be removed, and whether the segregated soil would require disposal in a RCRA landfill or incineration. The project was under severe time constraints as well due to rapid encroachment of residential development on neighboring properties.

Upon completion of the planning, the remediation was rapidly accomplished with approximately 4 months from mobilization to the site for sampling until the contaminated soil was shipped off site for disposal. Site closure with the Washington Department of Ecology followed soon after submittal of the project completion report.

Expedited Characterization and Remediation Approach

The USACE selected an approach using on-site, near real-time chemical analyses supplemented with a limited amount of off-site fixed-laboratory chemical analyses. Immunoassay (IA) analytical techniques (EPA Methods 4041 and 4042) were used on site. The on-site analysis was designed to support in-field decisions regarding further characterization, removal, waste segregation, and waste disposal. The process of reviewing existing data and developing a data collection program that used in-field data collection and interpretation to drive further investigation is similar to the U.S. Department of Energy's Expedited Site Characterization (ESC) process. This remediation integrated removal and disposal activities into the field-based decision making procedures. This additional efficiency allowed the test plot to be remediated and available for unrestricted use in a short amount of time.

Two decision matrices were developed during project design, one for the focused removal of the buried pesticides and one for the sequential characterization and excavation of the shallow-occurring pesticides. These matrices combined a conceptual site model for the site with a means to quickly interpret the upcoming investigation data. The decision was based on the hypothesis that contamination would not migrate more than 9-12 inches deeper from where it was initially located in the soil. The output of the decision process on site was two soil removal and segregation plans. Of the two processes, the sequential characterization matrix shown in Figure 1 is described in the most detail in this paper.

By using ESC, the design and field teams focused on filling the data gaps that drove key decisions. Based on the analytical results at each level in the decision matrices, determinations were made for analyzing additional samples by on-site or fixed- laboratory tests. Using a combination of the two types of testing, the extent of contamination above the removal action levels was delineated. A site map showing the removal plan was generated using the decision matrix and presented as a 3-dimensional bar chart generated from a spreadsheet program. By developing decision matrices ahead of time, field personnel had the ability to interpret data at the site and make characterization and removal decisions in the field, with no need to demobilize from the site until the characterization and removal work was completed. The data collected during the field effort allowed the team to determine how much soil to remove from each location, as well as how to handle and dispose of the soil removed from each location. Since incineration costs about 10 times more than landfilling, soil segregation was important to controlling project cost.

Sampling Approach

Undisturbed soil characterization samples were collected using direct-push technology so that samples would represent their specific grid and depth interval. In addition, plastic sleeves were used with the direct-push system. The sleeves, which are easily cut into segments and capped, provided easy sample handling and helped prevent cross-contamination between samples.

The site soil, which had been imported and placed in an excavation to form the test plot, was a silty topsoil. A direct-push sampling pilot test was conducted and indicated that the push probe easily and quickly advanced to six feet below ground surface, the maximum depth anticipated for sampling. Soil recovery in the push probe was approximately 90% during the pilot study.

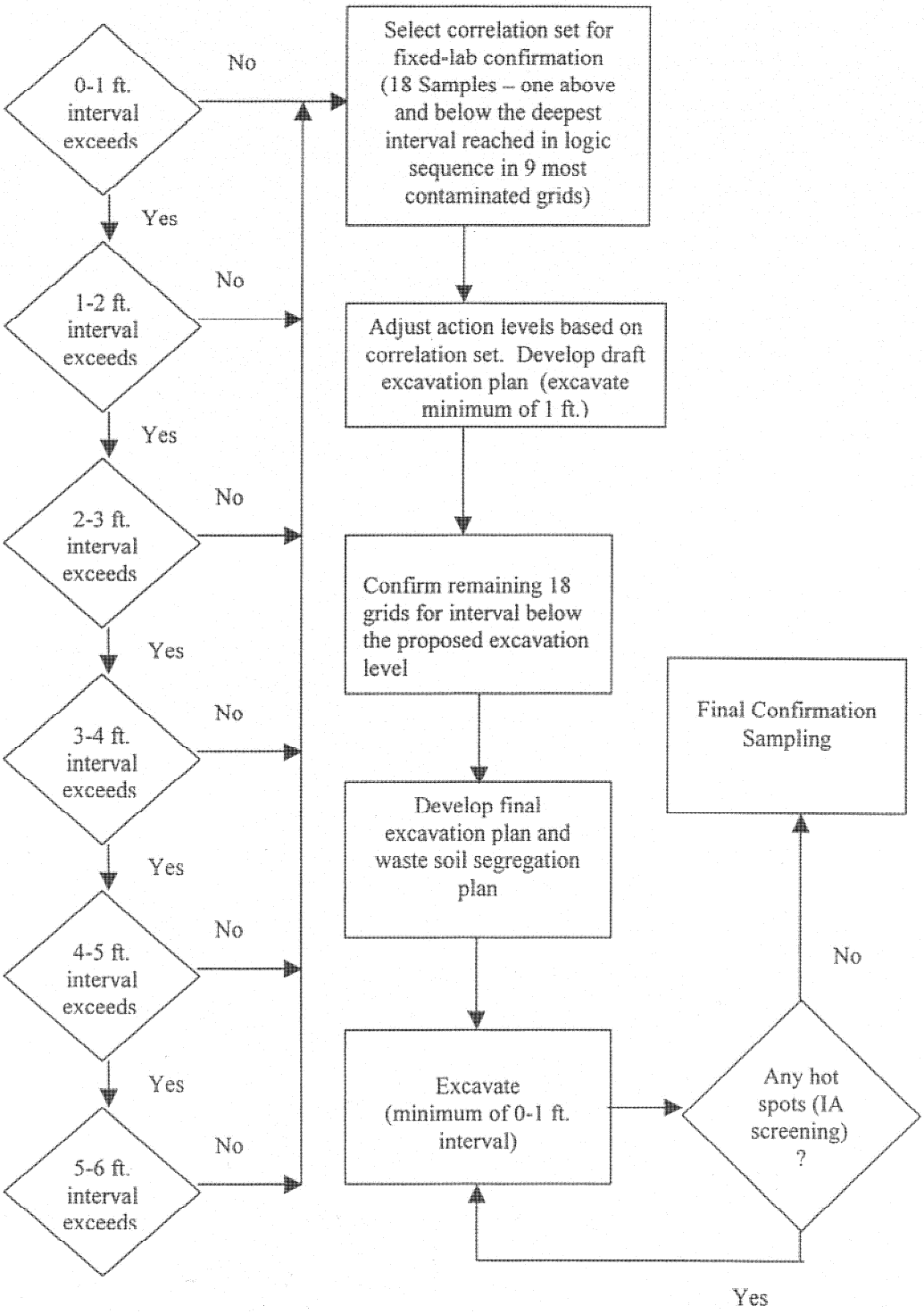

Figure 1. Sequential Vertical Characterization Screening With Immunoassay Analysis and Development of an Excavation Plan with 27 Direct-Push Borings

During characterization soil samples were collected to a depth of six feet from 27 push locations in one day. This produced the potential for approximately 160 samples to be analyzed in two days with each of the two IA screening tests. The direct-push probe met refusal in only one location at approximately 5 feet below ground surface where dense native soil was encountered.

Chemical Characterization Strategy

The compounds of concern included chlorinated pesticides of both the cyclodiene and DDT classes, carbamates, paraquat, and organophosphorus pesticides. In the State of Washington, waste designation analytical effort is based on constituent concentrations for toxics in addition to the toxicity characteristics established through the

Toxicity Characteristic Leaching Procedure (TCLP). In some cases particular compounds were of interest for site cleanup, e.g. dieldrin with a clean up level at 0.062 mg/kg. In other cases a compound was of particular relevance to waste designation, e.g. endrin, which had to be tested by TCLP if the constituent concentration in excavated soil exceeded 0.4 mg/kg (based on the "times 20 rule"). The "times 20 rule" determines the minimum constituent concentration that has the potential to exceed the waste designation level in the TCLP extract. On the other hand, the endrin soil concentration could be as high as 0.9 mg/kg, without a cleanup action if the soil did not require excavation due to another contaminant. Because the analytical costs were estimated at nearly a thousand dollars per sample if tests were run, an alternative analytical strategy was selected to minimize costs. Since characterization efforts often return undetected results for a majority of the analytes, the cost per piece of critical data would have been exceptionally high.

The possibility of having large concentrations of one pesticide masking the presence of another compound of interest at trace levels had data quality ramifications. Additional compounds such as 2,4'-DDT and paroxon that are not part of standard analytical target lists were considered in order to account for their potentially significant contribution to the overall cleanup decisions and Washington State waste designation results.

Several key analytes were selected to be measured as indicators for the site characterization effort. The indicators selected were also amenable to analysis by available immunoassay tests. The field IA tests are accurate in the range of concentrations relevant to clean-up decisions. For soils with concentrations far above the clean-up levels, a "greater-than" estimate was adequate. Using the IA analyses for the indicator compounds reserved the fixed-laboratory analytical effort for confirmation of site clean-up and classification of certain wastes. In both of these efforts, high quality data were necessary to support the conclusions. Used this way, the fixed-laboratory methods were optimally useful, avoiding analytical budget being wasted with poor quality data.

The immunoassay tests have inherent limitations. They are sensitive to whole classes of pesticides and a compound of high toxicity at low concentrations may be masked by the presence of higher concentrations of compounds of less importance to site closure. On the other hand this cross-sensitivity allowed rapid screening of soil samples to identify the boundaries of the gross contamination. Also, because the detection limits for some tests were in the range of the cleanup standards for the most toxic compounds, these tests were also useful to target areas needing further excavation prior to closure sampling. Tables 1 and 2 summarize the sensitivity of the two class-sensitive immunoassay tests used for this project to individual compounds. The sensitivity is expressed as a detection limit.

Table 1. Immunoassay Sensitivity for the Cyclodiene Reactivity Group

Constituents	LLD (ppm)
Dieldrin	0.006
Aldrin	0.02
Heptachlor	0.006
Chlordane	0.01
Endosulfan I	0.006
Endosulfan II	0.006
Endrin	0.006
Toxaphene	0.2
Gamma - BHC	0.6
Alpha - BHC	2
Delta - BHC	2

LLD = lower limit of detection

Table 2. Immunoassay Sensitivity for the DDT Reactivity Group

Constituents	LLD (ppm)
4,4’ DDT	0.04
4,4’ DDD	0.01
4,4’ DDE	0.2
2,4’ DDT	4
2,4’ DDD	0.4
2,4’ DDE	3
DDA	0.002
Chloropropylate	0.007
Dicofol	0.1
Thiobencarb	5
Diclofop	70

Sampling and Analysis Logistics

Proper sample handling after push probe collection was critical to data quality. Push probe sleeves filled with the soil samples were covered with aluminum foil or other opaque materials to prevent photodegradation of DDT and its photoreactive daughter compounds. Based on the need for high soil sample production rates, for the sequential characterization effort the team selected coning and quartering within 1/2 gallon clean-certified jars for homogenization of samples prior to splitting. The team stored the jars in sample refrigerators in the on-site laboratory trailer until they were homogenized and analyzed. The team used stainless steel bowls for other samples like final confirmation sampling, when the production rate of samples was less than 40 per day. Once homogenized, samples were immediately placed in sample jars and stored in the refrigerators to await on-site analysis or shipment to an off-site fixed laboratory for analysis.

During the sequential characterization with the direct-push borings, 116 of the possible 160 samples analyzed for both cyclodienes and chlorophenyl ethanes. A set of fixed- laboratory confirmation samples was also taken from this group to develop a correlation with fixed-laboratory results and to adjust IA action levels as necessary. Then fixed-laboratory confirmation samples were analyzed for the remaining grids to make sure that the draft excavation plan developed from the sequential characterization was valid for the other pesticides of concern. For the correlation and excavation plan confirmation, a total of 42 of the 116 samples analyzed by IA were analyzed for at least one of the parameters by fixed-laboratory analysis. Three field chemists were utilized for two days to complete the sampling and analysis. Two field engineers assisted with the sampling supervision, sample handling and homogenization on the first day.

During the soil removal, the areas with suspected deep burial of pesticides was excavated first, followed by remedial confirmation sampling for IA analysis and selected fixed-laboratory analyses. Following the excavation of the rest of the site additional IA samples were collected to evaluate the completion of removal and identify grids that could be sampled for closure with fixed-laboratory analysis. Hot spots located in the floor and sidewalls required hand excavation to reduce the concentrations to an acceptable level. The cleanup decision rule was based on the 95% upper confidence limit on the mean concentration. Some individual samples were analyzed by the fixed laboratory rather than immunoassay to avoid known interferences in a particular area of the site. The total number of analyses needed for the closure-sampling phase was 98 IA samples, some for only one IA test, and 31 fixed-laboratory analyses.

For waste characterization, most of the designation decisions were based on the fixed-laboratory analyses performed during characterization. Three specific IA tests were used to screen some miscellaneous waste types at the site. Six composite samples involving multiple pesticide and metals parameters were used to characterize particular 20 cubic yard waste soil roll-off bins. A majority of the waste was determined not to be a hazardous waste based the TCLP test. Endrin proved to be the critical compound in that determination.

The immunoassay tests are most accurate and precise at the mid-calibration range. A modification of the standard sample weight and extraction solvent volume was used in order to allow a single extraction to create extract for both the cyclodiene test and the DDT tests. The calibrations were adjusted so the midpoints were near the action levels. Table 3 shows the calibration ranges used for this project (columns 2 through 4) compared to the site action levels.

Table 3. Immunoassay (IA) Calibration Range, Decision Levels and Range of Characterization Results

	Low	Middle	High	Site Cleanup Level (mg/kg)	TCLP Waste Designation (X20 Rule – mg/kg)	Initial IA Action Level (mg/kg)	IA Range Observed (mg/kg)
Dieldrin	0.018	0.086	0.512	0.062	None	0.08	0.01 – 3.3
Endrin	0.018	0.086	0.512	24	0.04		
α-Chlordane	0.040	0.20	1.20	0.77	0.6		
DDT	0.8	4.0	40.0	2.94	None	5	0.1 – 290

For the WTFREC project cross-sensitivity and the potential for multiple reactive compounds being present in a sample made the "IA Action Level" a significant unknown at the outset of the project design. The calibration ranges needed for the tests were initially estimated based on the previous site data and the site cleanup levels. In order to refine the estimation, four samples were collected and analyzed by both immunoassay and GC/MS. This correlation study indicated that an optimized IA action level for the cyclodiene test could be set at 0.08 mg/kg and for the DDT test could be set at 5 mg/kg (Table 3).

At the outset of the characterization effort, critical samples collected to establish the contours for excavation were confirmed with fixed laboratory results, providing a similar correlation data set. As the sampling proceeded to depth at the site, the compounds present changed. Due to the interferences (cross-reactivity) it was necessary to modify the action level when the post-excavation samples were being collected (see paragraph below regarding IA and fixed-laboratory correlation). The new action level during the screening analysis prior to confirmation sampling was set at 10 mg/kg for the DDT test.

The IA action levels were used with continual revision and adaptation. The action level for cyclodienes was complicated at the excavation boundary because of the coexistence of endosulfan with very low, but critical, levels of dieldrin. High cyclodiene results were also attributed in one area to the presence of toxaphene, a chlorinated camphene, multicomponent pesticide. The action levels for endosulfan and toxaphene were relatively high, so its presence effectively masked dieldrin concentrations in the range of interest. Once this was known, the immunoassay testing was terminated for that area and only fixed-laboratory results were used to refine the horizontal excavation boundaries.

Immunoassay Calibration

Because the IA tests needed to function in a quantitative mode rather than a "less-than, greater-than" mode, the logarithmic response of the tests was accommodated with a calibration routine set up in a spreadsheet. Log-transformed data were regressed linearly to establish a calibration curve. Calibration was performed using a control with each batch of fifteen to twenty samples with duplicate analyses of calibration standards at each of three concentrations and a blank. An example calibration plot is shown in Figure 2. The manufacturer provides one form of the IA kits that uses calibration curves stored in a field-portable colorimeter. However, for this project, the design team chose the simpler kits and the spreadsheet-based calibration because of the more rapid analytical sequence available in that format of the kits.

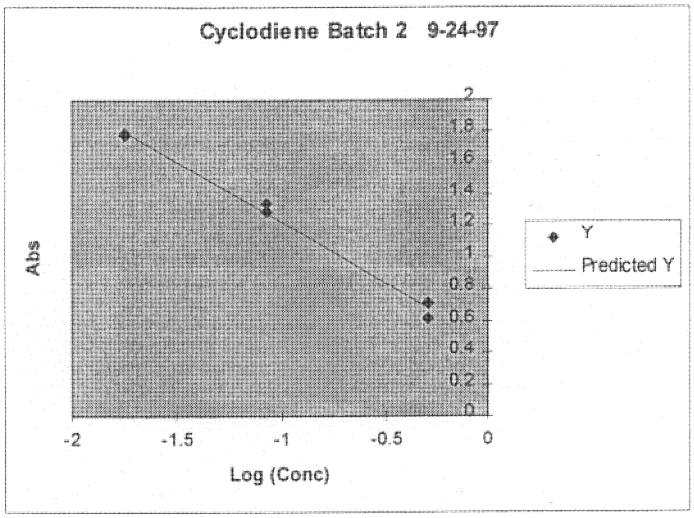

Figure 2. Cyclodiene Calibration

Immunoassay and Fixed-Laboratory Correlation

Given the complexity of the mix of pesticides found at this site, it is not surprising that the correlation between the screening and fixed-laboratory results was not consistent. In particular, as the extent of excavation wasreached, the mix of compounds affecting the tests changed. The DDT kit action level was boosted up to 10 mg/kg, to account for the new correlation. The cyclodiene test results at the periphery of the site were primarily affected by pesticides with relatively high clean-up levels, such as endosulfan. Therefore the responses of the critical compounds, dieldrin and endrin were being masked. A plot of the comparative results during the sequential characterization phase is shown in Figures 3 and 4. In general a pattern of occasional high bias by the IA tests is apparent, as expected due to the cross-reactivity and numerous compounds. A few cases of low bias are apparent and this mostly occurred at higher concentrations that were not in the range of a critical decision. The slope of the apparent correlation is not at 1.0 because the IA test calibrations are intentionally biased by 100% to avoid false negatives when used in the "less-than, greater-than" mode. The use of IA action levels modified by use of a correlation set of fixed-laboratory analyses compensated for this bias.

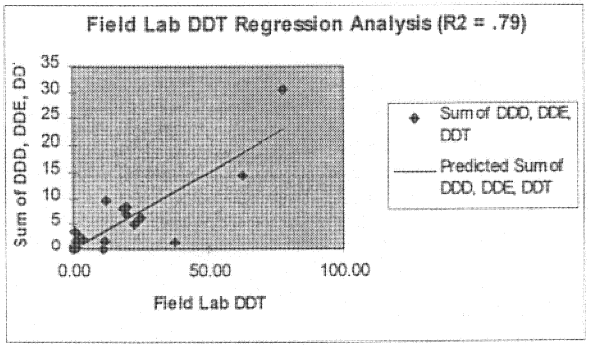

Figure 3. 1A and Fixed-laboratory Correlation

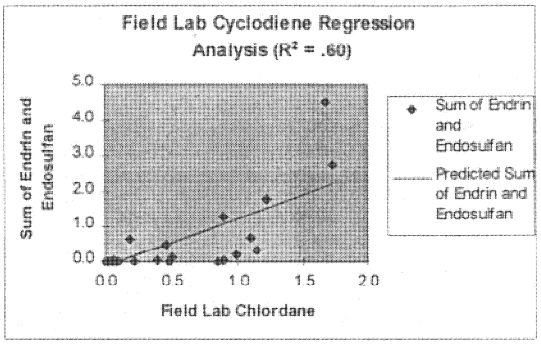

Figure 4. IA and Fixed-Laboratory Correlation

Quality Control

Ten percent of the field samples were collected in duplicate. Also, during the preparation of samples additional laboratory duplicates were extracted and analyzed. The duplicates generally performed very well (Figures 5 and 6). With each batch of analyses a quality control (QC) sample with known solution concentration was analyzed. The solution was produced with an extraction of the soil-matrix performance evaluation sample sent to the fixed laboratory containing a set of the analytes of interest at a concentration equal to the clean-up standard. Figures 7 and 8 show the control sample results. The QC sample served well to target batches that had analytical anomalies and required corrective action. The 100% positive bias of the kits is evident in the average recovery of the QC samples.

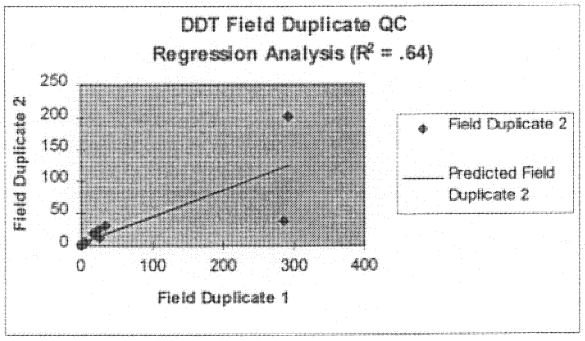

Figure 5. IA Field Duplicate Correlation

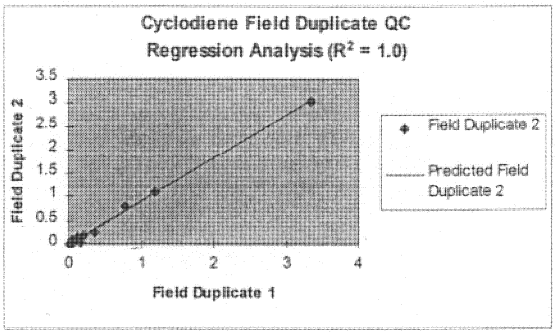

Figure 6. IA Field Duplicate Correlation

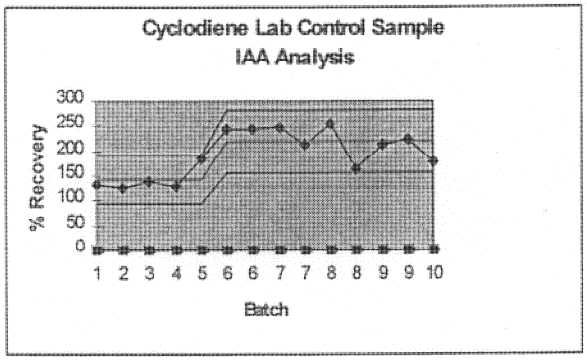

Figure 7. IA Control Chart

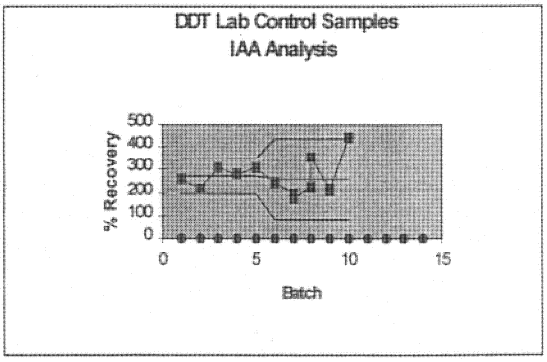

Figure 8. IA Control Chart

Summary

On-site immunoassay screening for cyclodiene and chlorophenyl ethane pesticides was successfully used at the WTFREC test plot remediation to expedite the soil characterization. The US Army Corps of Engineers design

team selected a characterization approach using on-site, near real-time chemical analyses supplemented with a limited amount of off-site fixed-laboratory chemical analyses. The on-site analysis was designed to support in-field decisions regarding further characterization, removal, waste segregation, and waste disposal. Using fixed-laboratory results to correlate the immunoassay results, the action levels for the field analyses were continually updated and adapted to site conditions encountered. The level of effort for the relatively expensive fixed-laboratory analyses was optimized through this approach. The amount of soil sent to treatment was also minimized. Following the remedial action, the site was successfully closed with the Washington Department of Ecology.

DEVELOPMENTS IN BIOTECHNOLOGY FOR ENVIRONMENTAL ANALYSIS

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Numerous advantages associated with immunoassays have made this technology the fastest growing analytical method in the diagnosis and management of disease. Immunoassays, along with chromatographic techniques, each having its own merits, are routinely used in clinical laboratories in the detection and quantification of biomolecules. By using complementary technologies, the clinical industry has been able to provide better quality results at a lower cost. Immunoassays are proving to be sensitive, accurate and cost-effective analytical tools for detecting many environmental contaminants. Once demanding expert skills, environmental immunoassays have now been simplified through automation and streamlined protocols. The routine acceptance of immunoassays and other biotechnology-based tests will depend on understanding the innovation behind the technologies, thereby allowing the full benefits of these new technologies to be applied to environmental analysis.

As we enter the 21st century, we will continue to see improvements in immunoassay automation and quality assurance procedures, ever-decreasing detection limits, and simplified sample processing methods. Multiple analyte technologies for the simultaneous measurement of two to four analytes are possible using DELFIA (dissociation-enhancement lanthanide fluoroimmunoassay). DELFIA is based on time-resolved fluorometry of lanthanide compounds such as europium. Four different toxicants in one sample are analyzed by using four different lanthanide labels each having distinctive fluorescence spectrum. This technology could allow for the ultrasensitive detection of polychlorinated biphenyls, polyaromatic hydrocarbons, and dioxins, simultaneously, in one measurement.

Discovery of the Ah receptor provided a key to understanding the molecular mechanism of dioxin toxicity. The Ah receptor is a ligand-activated transcription factor present in humans and animals that mediates most, if not all, of the harmful effects associated with exposure to these compounds. Once in the body, dioxin-like compounds bind to Ah receptors and alter transcription of genes encoding for estrogen receptor, tumor necrosis factor and transformation growth factor, among other genes. How tightly or loosely these compounds bind to the Ah receptor determines their toxicity. The Ah receptor is “nature’s perfect device” for testing these sorts of compounds. Many laboratories, worldwide, are evaluating cell-based Ah receptor assays as a cost-effective means to detect dioxins and furans. Genetically engineered Ah receptor is also being developed into an analytical tool which delivers dioxin analysis in a kit that can be packaged and shipped throughout the world.

Many of the toxicants that are routinely tested for in environmental samples (such as soil, sludge, and oil) eventually end up in the food chain. Severe restrictions on food trade were recently implemented in Europe and other countries after discovering PCBs and dioxins in food exported from Belgium. Testing food samples for PCBs currently costs about $200 using GC/MS and turnaround times are long. By using immunoassay technology and GC/MS analysis combined, a program was established that reduces the cost of testing 5 fold. Over 50 samples were analyzed in one day by two technicians in a study performed in Belgium, clearly demonstrating the “high throughput” testing capability of this technology. The study also demonstrated that correlation (R^2 value) between the immunoassay results and GC/MS was greater than 90 percent.

This is an exciting and diverse field built around the elegance of biological processes. We look forward to participating in a technology that connects so many disciplines. The adaptation and integration of new technologies for environmental analysis holds great promise for those who participate.

INORGANIC ANALYSIS

MONITORING LEAD CONCENTRATIONS IN SOIL BY ANTI-CHELATE FLUORESCENCE POLARIZATION IMMUNOASSAY

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ABSTRACT

Fluorescence polarization immunoassays (FPIA) provide a versatile method for measuring lead concentrations, using antibodies that bind selectively to the ethylenediaminetetraacetic acid (EDTA) complex of lead(II) and a fluorescent analog of that complex (termed a tracer). These reagents are used to configure FPIA tests that detect ionic lead(II), in the form of its EDTA complex, with high sensitivity and specificity. This FPIA technique is applied here to the measurement of lead in nitric acid extracts from soils, in Toxicity Characteristic Leachate Procedure (TCLP) extracts and in extracts obtained by direct treatment of soils with aqueous EDTA.

Assays are performed in disposable test tubes, by mixing an aliquot of aqueous extract with a buffered solution containing excess EDTA and the tracer. Antibody is then added and the tube is allowed to stand for 30 minutes before reading the polarization. The dynamic range of the assay is 0 - 50 ppb and the limit of detection is below 1 ppb. Cross reactivity with non-target metals is very low. Of sixteen metal ions tested, mercury(II) shows the highest cross reactivity (0.37%) with aluminum(III), iron(III), calcium(II) and magnesium(II) all exhibiting cross reactivities of 0.15% or lower.

Aliquots of dried, sieved soil (5 grams) were extracted with 50 mL of 1 M nitric acid for 1 hour then the extracts were analyzed by flame atomic absorption spectroscopy (AA) and by FPIA. Extracts were diluted by 2,000-fold to 20,000-fold to bring lead concentrations into the dynamic range of the immunoassay. FPIA results for 138 soil samples correlated closely ($r^2 = 0.96$) with the AA values, which ranged from extract concentrations of 0.2 ppm to over 300 ppm.

From the above soils, 15 samples were selected that had the highest lead content and aliquots of these were extracted for 18 hours with 100 mM acetate buffer, pH 4.93, at a ratio of 20 mL extraction fluid per gram of soil. The lead concentration in the supernatant was then measured using the FPIA. 6/15 samples gave extract concentrations at or above 5 ppm, i.e. failed the TCLP for lead. Iterative studies of selected samples using extraction buffers containing varying concentrations of EDTA, performed at a fixed ratio of soil:extractant of 1:20 and a fixed extraction time of 15 minutes, were used to empirically identify an EDTA concentration that mobilized the same fraction of soil lead as did an 18 hour extraction with 100 mM acetate. Aliquots of the 15 soil samples were then extracted for 15 minutes using that concentration of EDTA and lead in the resulting supernatant was determined by FPIA. The (EDTA extraction + FPIA) procedure correctly identified 9/9 soils that passed the TCLP and 5/6 samples that failed.

These results illustrate the potential for simple, rapid, field portable immunoassays that can measure acid extractable lead concentrations in soil and that can predict whether a soil sample will pass the TCLP test for lead.

INTRODUCTION

Antibodies that can detect subtle structural differences between (and thus bind differentially to) chelates formed from two different metals and the same chelating agent were first described in 1985[1] and have been used to develop enzyme linked immunosorbent assays (ELISA) for measuring indium(III)[2] and cadmium(II)[3] in water. Similar antibodies to an EDTA chelate are used here to measure lead(II), by allowing Pb-EDTA (formed by addition of excess EDTA to the sample) to compete for a limited concentration of antibody binding sites with a fixed concentration of Pb-EDTA covalently linked to fluorescein. The fluorescence polarization method is a homogeneous immunoassay technique that was first applied to the study of solution phase antibody-antigen interactions in 1973[4] and has been used extensively in the determination of various low molecular weight organic analytes[5,6]. An FPIA test for lead is performed by mixing an aliquot of aqueous sample with (i) a buffered solution containing excess EDTA and a fixed concentration of tracer; then (ii) a buffered solution containing a fixed concentration of anti-Pb-EDTA antibody. After brief incubation, the polarization of the signal emitted when the solution is excited with plane polarized light is determined.

METHODS

Reagents. Polyclonal antibodies to the Pb(II)-EDTA complex were produced in New Zealand White rabbits immunized with a bovine serum albumin conjugate of Pb-EDTA. The fluorescent tracer was obtained by reaction of fluoresceinamine isomer I with an EDTA derivative bearing
a -1-*para*-benzylisothiocyanate group, followed by complexation with $Pb(NO_3)_2$. Standards were prepared by dilution of a 1,000 ppm Pb AA standard (Aldrich) into 1 M nitric acid.

Samples. Soil samples were collected from residential and agricultural areas throughout Wisconsin, including some with a prior history of lead arsenate application. Soil pH ranged from 4.5 to 8.2 with a mean of 6.8. Organic matter ranged from 0.9% to 39.5% with a mean of 4.4%. Soil texture ranged from Loamy Sand (84% sand, 11% silt, 5% clay) to Loam (30% sand, 51% silt, 19% clay).

Acid extracts. Soil samples were dried and sieved through a 2 mm screen before extraction. A 5 g aliquot of dried, sieved soil was shaken with 1 M nitric acid (50 mL) for 1 hour then filtered through Whatman #2 filter paper. (To allow for the 10-fold dilution factor, the soil lead content is calculated by multiplying the measured extract concentration by 10).

TCLP extracts. Forty TCLP extracts with lead content ranging from undetectable to approximately 700 ppm were obtained from a sample archive at the Wisconsin State Laboratory of Hygiene.

EDTA extracts. Aliquots of dried, sieved soil (200 mg) were weighed into 5 mL disposable test tubes. To each tube was added 4.0 mL of a buffered EDTA solution, then the tube was sealed and mounted on a shaker. After agitating the contents of the tube for 15 min. at room temperature, the suspension was allowed to settle for 1 - 2 min.

Immunoassay procedure. An aliquot of the soil extract was diluted with distilled water then an aliquot of the resulting dilute extract (10 µL) was pipetted into a 5 mL disposable borosilicate glass test tube containing 1.0 mL of assay reagent 1 (25mM HEPES + 25 µM EDTA + 2.5 nM Pb-EDTA-Fluorescein, pH 7.4). Assay reagent 2 (buffered solution of anti-Pb-EDTA antibody) (20 µL) was then added to the tube. After standing at room temperature for 30 minutes, the tube was transferred to a fluorescence polarization analyzer and duplicate polarization readings were taken and averaged. Fluorescence polarization measurements were made using a Sentry FP analyzer (Diachemix Corp., Grayslake, IL) with excitation at 485 nm and monitoring emission at 505 nm. The lead content of the extract was calculated from a standard curve, obtained by plotting mean polarization against lead concentration for the five calibrators and fitting the results to a single exponential curve by non-linear regression analysis. Samples that were off-scale on initial analysis were diluted 10-fold with distilled water and re-analyzed.

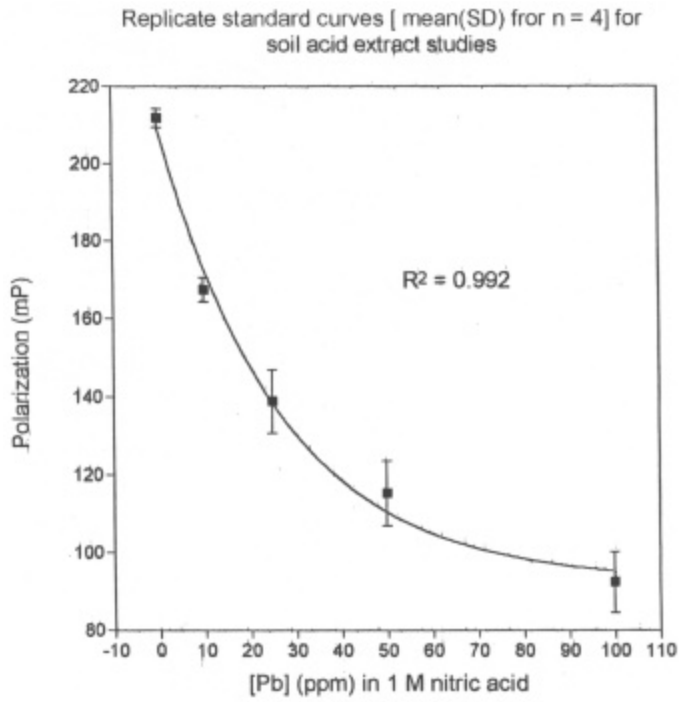
RESULTS

The dynamic range of the FPIA for aqueous, ionic lead(II) under conditions that minimize sample dilution is 0 - 50 ppb, with a limit of detection below 1 ppb. To bring extract lead concentrations into the working range of the immunoassay, sequential dilution steps were incorporated into the assay procedure such that final dilutions of extract into the assay were from 1,000-fold to 20,000-fold. Interference studies with sixteen potentially cross-reactive metals showed minimal response to non-target metals. The strongest cross reactions were with mercury(II) (0.37 %) and silver(I) (0.19 %). Cross-reactivity with iron(III) and aluminum(III) is below detection limits (less than 0.05 %) and that with calcium(II), magnesium(II), zinc(II), copper(II), manganese(II), cadmium(II) and chromium(III) is below 0.15 %. The assay is therefore both very sensitive and quite specific for lead(II).

An assay standard curve and correlation data for 104 soil samples that had an acid extractable lead content close to the action level of 100 ppm soil content (10 ppm extract concentration) appear in the Figures. Results obtained by immunoassay correlated well with those obtained by AA analysis of the same extracts. Similarly, immunoassay results were in good agreement with the corresponding ICP-AES data for conventional TCLP extracts. For a limited number of samples, a prototype brief, direct extraction of the soil with a buffered solution of EDTA, when combined with FPIA analysis of the resulting extract, gave results that correlated with those obtained by conventional TCLP extraction.

SUMMARY

Results obtained to date with an FPIA test for ionic lead(II) suggest that it may be used to measure lead concentrations in a variety of extracts obtained by treating soil with mineral acid, with mildly acidic acetate buffer



(TCLP) or with buffered EDTA solution.

The FPIA test requires few skills other than pipetting and consumes few disposables other than test tubes, pipet tips and reagents. The extract is the only waste product remaining after the assay that presents any safety issues - the FPIA reagents themselves are innocuous. The Sentry FP instrument used to read the assay is rugged, simple to operate and field portable, being interfaced to and powered by a notebook computer.

We conclude that the anti-chelate FPIA test offers a simple, flexible means of measuring lead concentrations in soil that is potentially applicable in a variety of screening and monitoring situations.

ACKNOWLEDGMENTS

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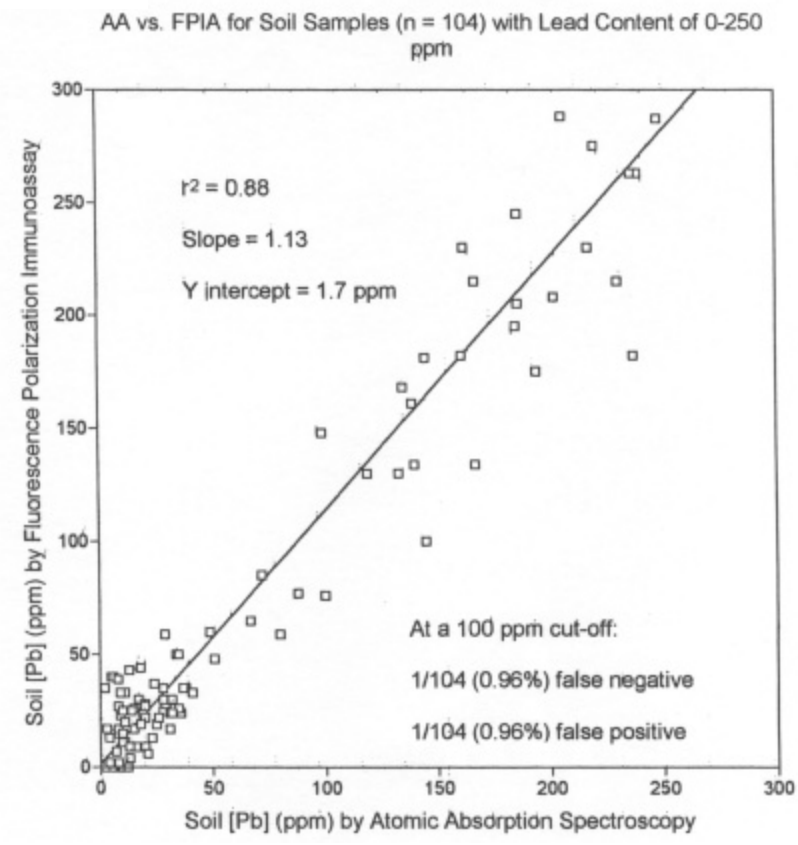
The authors thank Dr. William Sonzogni and Dr. Al Clary, Wisconsin State Labor- atory of Hygiene, Madison, WI for kindly providing the TCLP extracts and ICP-AES data for their lead content.



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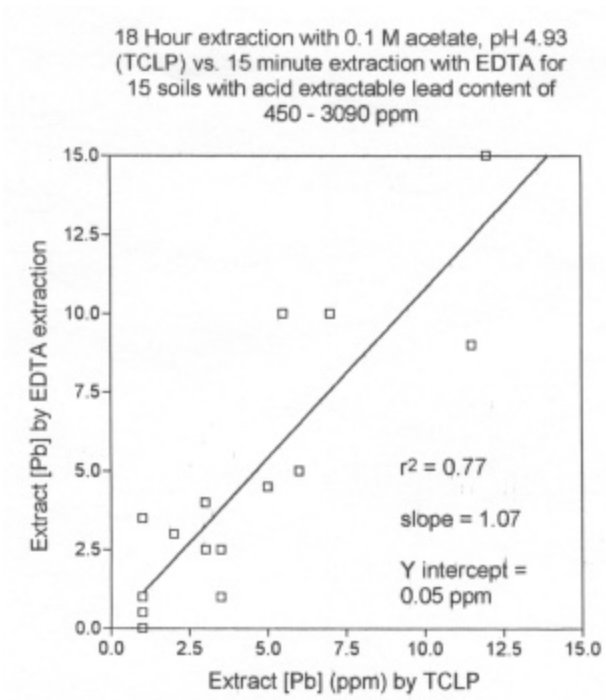

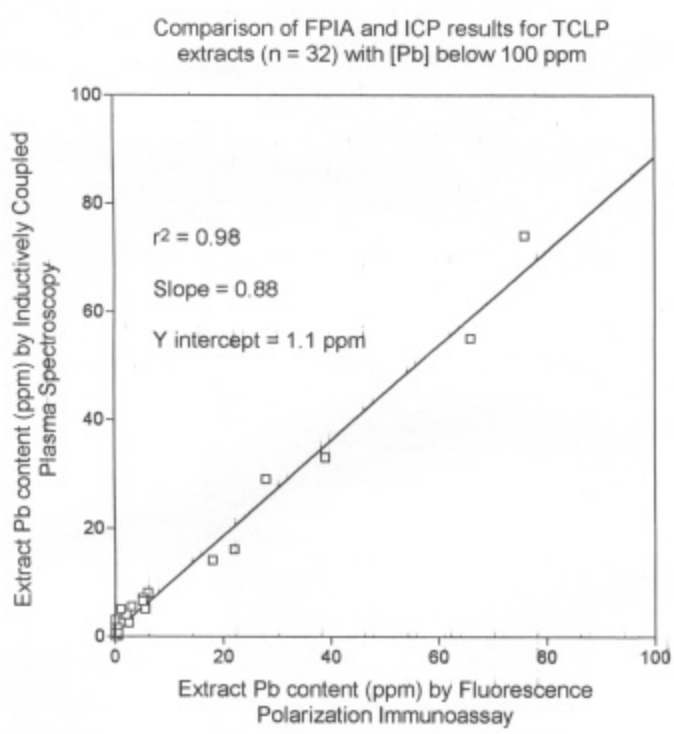

TAKING MERCURY ANALYSIS INTO THE 21ST CENTURY WITH SPECIATION

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ABSTRACT

Speciation is quickly becoming the analytical standard of the 21st century. While there are several techniques available for the analysis of total mercury, there is a need for those that are capable of providing species-specific information. This presentation will discuss how the integration of two EPA Methods, 7473 and 3200, is being used for the analysis of mercury species. Method 7473 is a method designed for the analysis of total mercury in both liquid and solid samples, while draft Method 3200 is a mercury species extraction procedure. Use of Method 7473 for analysis of the extracts from Method 3200 has proven to be an efficient mercury speciation tool.

INTRODUCTION

Method 7473 has been developed for the analysis of total mercury in a variety of matrices. Its unique processing of the sample by thermal decomposition, amalgamation, and atomic absorption spectrometry allows for direct analysis; a discrete sample preparation step is not required. Research is ongoing to extend Method 7473 for mercury species classification by use of a front-end class-selective extraction procedure. The unique ability of Method 7473 to analyze samples directly allows for mass balance studies in the extracted fractions as well as in the solid material.

Draft method 3200 is a sequential extraction procedure that is being developed to classify mercury species into two groups: "extractable" and "non-extractable". The "non-extractable" mercury species are operationally defined and include those species that are the least bioavailable. The "extractable" mercury species are operationally defined and include those species that are the more bioavailable and/or toxic forms of mercury. An option is given in Method 3200 to further subspeciate the "extractable" mercury into "extractable inorganic" and "extractable organic" mercury. Table 1 provides examples for the operationally defined speciation of Method 3200.

Table 1. Examples of the operationally defined species in Method 3200

Total Mercury		
Extractable Mercury		***Non-Extractable Mercury***
Extractable Organic Mercury	**Extractable Inorganic Mercury**	
CH_3HgCl CH_3CH_2HgCl	$HgCl_2 \bullet Hg(OH)_2$ $Hg(NO_3)_2 \bullet HgSO_4$ HgO	HgS $Hg^{(0)}$ or $Hg^{(0)}/M$[a] Hg_2Cl_2
		Hg^{2+} (complexed)[b]

[a]This represents a mercury-metal amalgam.
[b]Certain inorganic mercury species may be present in both categories.

Several alternative extraction procedures have been evaluated. The most promising candidates include 10% ethanol + 2%HCl and 2M HNO_3. The extraction procedures have been tested on various matrices that have been spiked with the mercury analytes of interest. The procedures have also been validated by using a sample that is certified for both methylmercury and total mercury (Certified Reference Material (CRM) 580)). Table 2 provides the matrices and species of interest that have been investigated.

Table 2. Matrices and species of interest that have been evaluated for extraction of mercury by Method 3200.

Matrices	***Mercury Species***
Silicon	$HgCl_2$
"Clean" soil[1]	CH_3HgCl
Potting soil	C_2H_5HgCl
SRM 2709	HgO
CRM 580	Hg/Zn
	HgS

[1]This soil was thermally treated to remove a majority of the inherent mercury prior to spiking.

Table 3 demonstrates percent recoveries for spiked mercury species in the "clean" soil matrix using two different leach alternatives. Excellent recoveries were obtained for the "extractable" mercury species.

Table 3. Recovery of spiked "extractable" mercury species from the "clean" soil matrix.

Mercury Species	***10% ethanol + 2% HCl Recovery (%)***	***2M HNO_3 Recovery (%)***
$HgCl_2$	106 ± 15	93 ± 9
CH_3HgCl	104 ± 10	98 ± 26
CH_3CH_2HgCl	92 ± 18	79[1]

[1]Only one sample was quantified for CH_3CH_2HgCl spike; no uncertainty expressed.
Uncertainties expressed as 95% confidence interval for n=3.

Table 4 demonstrates percent recoveries for spiked mercury species in the potting soil matrix using two different leach alternatives. While good recoveries were achieved for the organic mercury species using both techniques, the 10% ethanol + 2% HCl was not able to fully recover the inorganic mercury spike. The incomplete recovery may be due to transformation of the spiked inorganic mercury to "non-extractable" mercury during the equilibration of

the mercury spike and potting soil matrix.

Table 4. Recovery of spiked "extractable" mercury species from the potting soil matrix.

Mercury Species	*10% ethanol + 2% HCl Recovery (%)*	*2M HNO_3 Recovery (%)*
$HgCl_2$	12 ± 6	86 ± 40
CH_3HgCl	89 ± 12	103 ± 2
CH_3CH_2HgCl	95 ± 15	NA

Uncertainties expressed as 95% confidence interval for n=3.

An alternative for subspeciation of the "extractable" mercury into "extractable inorganic" and "extractable organic" mercury is provided in Method 3200. Sulphydryl cotton fiber (SCF) is used as a solid phase extraction material that collects both the inorganic and organic mercury forms. The organic mercury and inorganic mercury can then be selectively eluted, as demonstrated in Table 5.

Table 5. The recoveries of target mercury species after solid phase extraction by SCF.

	CH_3HgCl	**C_2H_5HgCl**	**$HgCl_2$**
Pass-through	<1%	<1%	<15
Extractable organic mercury	96%	99%	<1%
Extractable inorganic mercury			98%
Residue (in SCF)	<1%	<1%	<1%

SUMMARY
EPA Methods 7473 and 3200 can be used in conjunction with one another to provide mercury speciation data. 10% ethanol + 2% HCl and 2M HNO_3 have been tested as alternative leaching procedures to selectively extract the more toxic and/or bioavailable forms of mercury. The "extractable" mercury can then be subspeciated into organic and inorganic forms of mercury using solid phase extraction with sulphydryl cotton fiber. Speciation by the 7473/3200 method pair is enabling mercury analysis for the 21st century.

RAPID TRACE METAL ANALYSIS OF HIGH SOLIDS WASTEWATER AND SLUDGE

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ABSTRACT
The current state of analytical instrumentation is lacking in the analysis of high solids wastewater and sludge. As a result, Pima County Wastewater Management (PCWWM) and the University of Arizona have cooperated in the development of a prototype instrument capable of analyzing high solids matrices both quickly and reliably. The current instrument utilizes a direct current plasma source (DCP) and a state-of-the-art echelle spectrometer fitted with a solid state array detector. The result is an extremely forgiving analytical technique capable of providing a simultaneous, multi-element fingerprint of contaminants in wastes. Furthermore, multi-element analysis is obtained quickly with minimal or no sample preparation, making this the fastest technique available for trace metal analysis of wastes. Samples ranging from drinking waters to wastes with solid contents of 4% are analyzed in

under two minutes for over 30 elements. In addition, the instrument costs less to produce and operate than an inductively coupled plasma (ICP) spectrophotometer, which is the most commonly used technique for trace metal analysis.

To date this instrument has been successfully used to monitor contaminants in drinking water, industrial and hazardous wastes, sludge, soil, and wear metals in lubricating oil. Quantitative performance is similar to ICP in regards to sensitivity and dynamic range and comparison data is available for a variety of matrices and SRM's. Another benefit of this configuration is the inherent possibility as a mobile spectrometer. Work is currently underway to develop a mobile unit which will greatly improve pollution monitoring capabilities and hazardous waste screening at onsite locations, thereby minimizing analysis turnaround time.

KEY WORDS
Direct current plasma (DCP), emission spectroscopy, charge injection device (CID), charge-transfer device (CTD), publicly owned treatment works (POTW), biosolids, wastewater, National Pollution Discharge Elimination System (NPDES).

INTRODUCTION
Operation of publicly owned treatment works (POTWs) is critical for controlling pollution and ensuring public health and safety. As a result, municipal treatment facilities routinely monitor wastewater, sewage and biosolids sludge from a variety of domestic and industrial sources having varying degrees of solids content. These varying sample matrices can create analytical challenges for the laboratory, particularly in the area of trace metal analysis, where sample homogeneity is a primary concern.

Throughout the past decade, environmental regulations have become increasingly stringent for wastewater compliance monitoring and as a result, the maximum allowable concentrations for pollutants discharged into the environment has decreased. This trend has forced POTWs to modify the ways in which wastes are monitored and controlled. No longer can these facilities simply monitor the waste stream as it enters the treatment plant lest they be at risk of violating their own NPDES permit should an exceedence occur. Fines imposed for violation of a regulatory permit can range from $25,000 per day, per pollutant up to $100,000 per day for repeat violations. Accumulation of pollutants in the sewer system can adversely affect the operation of POTWs by inhibiting normal operation of the biological treatment process. In addition, heavy metals are normally concentrated in the treatment plant sludge, which may limit the sludge acceptability for land application purposes. As a result, many POTWs have instituted aggressive pretreatment programs to aid in monitoring the waste stream entering these facilities. These programs consist of monitoring industrial discharge sites and educating the public in regards to contaminants allowed into the sewer system. In addition, contaminants are often monitored via sewer manholes to track pollutants to the source in what has become known as point source monitoring.

Pima County Wastewater Management (PCWWM) is located in Southern Arizona and currently operates two large-volume treatment facilities that are regulated under EPA's NPDES program. Effluents from these facilities are allocated for reuse programs around the greater Tucson area and discharged into the Santa Cruz River basin for natural recharge of the aquifer. In addition, digested sludge resulting from the treatment process is put to beneficial use as fertilizing material for local cotton crops or combined with mine tailings to provide organic material in previously barren locations. As part of the pretreatment program, a regional discharge facility was constructed where septage pumper trucks deposit waste at a central location. Various techniques capable of rapid trace metal analysis were evaluated for screening these wastes before discharging into the treatment system. Sample matrices ranged from domestic and industrial wastewater to sludge. Solid content ranged from total dissolved solids of 300 mg/L on treated effluents to 9% total solids on thickened sludge. In order to prevent unnecessary delays for septage haulers, emphasis was placed on quick analysis turnaround time for both qualitative and quantitative results. The ideal technique would require little or no sample preparation and would be able to provide a rapid, multi-element fingerprint of contaminants in the waste before the pumper truck left the facility, typically within thirty minutes.

Although many techniques are available for trace metal analysis, not all methods are suitable for high solids matrices. Atomic absorption spectrophotometers, both flame atomization (FLAA) and graphite furnace (GFAA), were quickly dismissed because of FLAA's sensitivity and GFAA's prohibitively slow analysis times. These techniques utilize monochrometers requiring sequential analysis of each wavelength and thus increase overall analysis time and labor. Energy dispersive x-ray fluorescence (EDXRF) was also evaluated but proved unsuitable for liquid wastes and slurries. Sample heterogeneity and extensive sample preparation make EDXRF unsuitable for rapid characterization. Inductively coupled plasma (ICP) was also evaluated as a result of the many favorable

features such as excellent sensitivity, multi-element capability, and ease of operation. The echelle optics and charge transfer device (CTD) detection used in many ICPs have resulted in extremely versatile instruments. Despite these features, ICP-AES has difficulty accommodating high solids and problems using ICP-AES for high solids are documented throughout the literature. The aspiration of high solids reduces nebulizer efficiency and creates such a large load on the plasma that it is often extinguished. These same effects also hinder ICP-MS and the linear range of many ICP-MS instruments is not suited for the high concentrations encountered in most wastes. In addition, these complex matrices often require intensive digestion and preparation techniques and are usually analyzed by standard additions, further increasing analysis time and cost. The use of direct current plasma (DCP) instruments has decreased significantly throughout the past decade as a result of ICP popularity. Early version DCP spectrometers suffered in comparison to ICP-AES in the area of spectrometer performance because of poor light throughput into the spectrometer and cumbersome operation. In addition, DCP typically produces fewer emission lines than ICP which places wavelength availability at a premium. As a result, commercial production of DCP instruments was briefly discontinued in 1993. However, one advantage afforded by DCP is the ability to accommodate high solids. This feature is largely due to the sample introduction system and the robust plasma source.[1,5]

EXPERIMENTAL

Since none of the techniques mentioned adequately addressed all of these needs, an alternative instrument was constructed incorporating the optimal features of each technique. As a result, many of the requirements previously mentioned have been met with the system described in this manuscript. The current configuration utilizes cross-flow nebulization for high solids capability, a robust DCP plasma source for atomization, and a state-of-the-art echelle spectrophotometer for measurement of wavelength emissions.

The DCP source consists of a three-electrode type consisting of two graphite anodes and a single tungsten cathode and is essentially unchanged from previous commercial versions. Various changes were designed into the sample introduction system in order to accommodate samples of varying solids content. A single pass Scott-type mixing chamber is fitted with a cross flow nebulizer for increased solids capability. The Scott spray chamber is preferred as the horizontal orientation allows for the use of an additional mirror assembly to be used for increased light throughput and improved sensitivity. In addition, sample injector tips of varying diameters are used to enhance performance on different matrices.[4] In order to facilitate optical alignment of the source, a miniature 1/3" CCD camera is placed inside the spectrometer to view the plasma position upon the entrance slit. All front end optics, including the plasma source, are mounted directly to the spectrometer entrance housing for better stability while minimizing the need for realignment.

As always, wavelength coverage and sensitivity are primary concerns when dealing with any form of spectroscopy. Sensitive ultraviolet performance is required for the analysis of elements such as arsenic, selenium and zinc as arsenic is routinely monitored at 189.04 nm and 193.7 nm making low ultraviolet performance critical to the successful determination of these elements. Furthermore, potassium determinations are performed at 766 nm, necessitating extended wavelength coverage for multi-element analysis. The current configuration offers simultaneous wavelength coverage from 170 nm - 800 nm while utilizing a single CID detector. In addition, the extended wavelength capability of the modified DCP echelle/CID often provides for analysis at multiple wavelengths per analyte. Studies utilizing CID and CCD detector technology coupled with echelle spectrometers have previously been described and have now become standard equipment on almost every commercially available ICP.[2,3]

Spectrometer performance of the echelle/CID is significantly improved over that of earlier version DCP instruments which utilized PMTs. The optical path of the modified DCP is diagramed in Figure 1. A quartz/calcium fluoride achromat lens is used for source imaging upon the 100 µm entrance slit. An electromechanical shutter is positioned between the entrance slit and collimating mirror to precisely control exposure times. A 17.5º quartz prism is used for cross dispersion while a ruled echelle grating with 54.5 grooves/mm and 45.5º blaze angle is utilized for high dispersion. The CID38 detector is a 512 x 512 pixel device and is housed in a cryostat cooled to -85ºC to minimize the effects of dark current. Individual pixel dimensions are 27 µm tall and 23 µm wide. The overall photo active area is 8.7 mm x 8.7 mm and contains a total of 262,144 detector elements. A toroidal mirror is used to focus the slit image onto the CID sensor. The fixed optical layout is essentially maintenance free, unlike PMT-based systems, which require critical alignment of exit slits. With the CID-based system, all wavelengths correspond to pixel coordinates and are digitally stored in software. The entire database is updated and adjusted in relation to the primary mercury wavelength of 253.65 nm. Therefore, all alignment is performed digitally within the software after a brief exposure to a mercury pen lamp. This is a substantial cost savings because alignment is

under software control and can be performed instantly and effortlessly without the need of a service call. The entire optical path is purged with argon to further remove entrained atmospheric air, which would otherwise degrade far-UV throughput. Additionally, the spectrometer is heated and under thermostat control to prevent misalignment from temperature fluctuations within the optics.

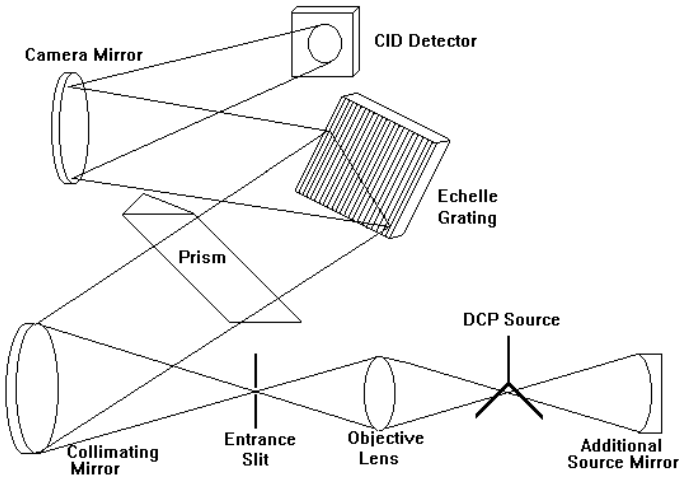

Figure 1. Optical layout of the CID echelle spectrophotometer.

RESULTS AND DISCUSSION

Results of this study demonstrate the ability of the modified three-electrode DCP to accommodate matrices with solids up to 2% with little sample preparation. Samples containing higher solids require screening to remove granular particulate which would otherwise impede sample uptake through the peristaltic tubing and nebulizer. Samples with solids >2% were subjected to either a two minute centrifugation, dilution, or filtration through a 5 µm membrane to remove particulates. Samples previously analyzed by ICP with difficulty were easily accommodated by the DCP. The ability to accommodate increased solids is attributed to the path in which the sample flows around the plasma core.[6] In ICP configurations, the entire volume of sample exiting the injector tube must pass through the center of the plasma. Under conditions of high solids, the plasma can become unstable and be extinguished. In all three-electrode DCP configurations, a large percentage of the aspirated sample flows around the plasma core, with only a portion being atomized. This results in increased solids capability but at the expense of decreased emission intensity. The use of an additional mirror assembly positioned behind the DCP source successfully increased the available emission signal by approximately 50%.

Viewing position with a three-electrode plasma is extremely temperature dependent as the plasma temperature is considerably hotter near the convergence of the two branches. Elements requiring higher atomization temperatures must be viewed from this region while easily atomized elements are adequately analyzed well below the plasma. As a result of this temperature dependence, simultaneous, multi-element determinations are performed at a compromised position somewhere below the plasma. Analytical performance is compromised as a result because many analytes optimally analyzed under light temperature excitation conditions are insufficiently atomized. The additional mirror assembly adequately addresses this concern as it allows the analyst to focus at two distinct regions of the plasma simultaneously, thus ensuring adequate atomization of all species present in solution. Alternatively, the analyst can choose to focus at the same plasma region, thus improving throughput at a specific wavelength. The 1/3" CCD internal alignment camera simplified optical alignment of the viewing position. Figure 2 depicts the plasma image on the entrance slit as viewed with the alignment camera.

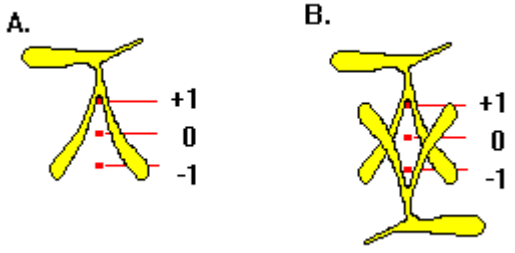

Figure 2. A) Available plasma viewing positions with standard DCP. B) Dual plasma viewing postitions available in the prototype DCP.

Perhaps the greatest benefit of the echelle/CID spectrometer is the ability to perform multi-wavelength analysis simultaneously. This feature is extremely advantageous when analyzing complex matrices where spectral interferences can be substantial. The ability to identify spectral interferences and select alternative wavelengths simultaneously is a tremendous advantage when screening wastes. The current database contains multiple

wavelengths for over 70 elements, making this technique far more versatile than either simultaneous or sequential PMT systems.

Quantitative performance of the modified DCP is comparable to an ICP in regard to sensitivity and dynamic range. Sensitivity for some elements is slightly less than that of current ICPs, which is presumably due to the decreased emission intensities of the DCP and the difficulty associated with purging the optics around the DCP source. However calibration ranges remain linear for up to five orders of magnitude, making this technique ideal for high-solids-analyses. The results indicate a high degree of accuracy, regardless of matrix and solids content. Extensive comparison data is available on a variety of matrices and standard reference materials (SRMs) but is too numerous to be included in this manuscript. Copies will be available at the presentation.

SUMMARY

The modified DCP equipped with an echelle/CID spectrometer has tremendous application for use in the screening of industrial wastes. The three-electrode DCP is capable of handling the challenges of high solids analysis. Samples that previously extinguished an ICP plasma are successfully analyzed using a DCP source. Overall analysis times were significantly decreased by minimizing sample preparation and by the ability to perform multi-element analyses simultaneously. A DCP can also be operated at a significant cost savings, as argon consumption rates are approximately 6.0 lpm compared to the approximately 12.0 lpm required by a typical ICP to maintain torch coolant. In addition, the lack of expensive quartz glassware makes operating a DCP far more attractive by reducing the cost of expensive consumable parts.

The sensitivity, accuracy and dynamic range of the modified DCP are comparable to conventional techniques and require significantly less sample preparation. Fully quantitative, multi-element fingerprints of contaminants are achieved simultaneously with unprecedented speed. A complete, multi-element fingerprint is typically obtained in under one minute, making this one of the fastest screening techniques available for complex sample matrices. The continuous wavelength coverage allowed by the echelle/CID spectrometer allows users to monitor multiple emission lines for any given element. This is in contrast to PMT-based spectrometers, which are purchased in either simultaneous or sequential configurations. Simultaneous PMT systems usually provide for analysis at a single wavelength and can be expensive, depending on the number of PMTs contained. Sequential PMT systems provide complete wavelength coverage but are inherently slow. The ability to view analytes and interferences simultaneously is a significant advantage when using a CID detector. Additionally, the echelle/CID system allows for choosing the best spectral lines for quantification at interference-free wavelengths. Interferences associated with emission of the plasma continuum is also less significant with DCP because many analytes are viewed well below the plasma thus improving spectral purity.

Another benefit of the DCP configuration is its inherent possibilities as a mobile spectrometer. The critical alignment required to operate a PMT spectrometer makes operation in a mobile laboratory impractical. A few manufacturers have attempted mobile ICPs with minimal success. Work is currently underway to develop a mobile DCP utilizing an echelle/CID spectrometer. The lower voltage requirements and reduced argon consumption make DCP more suitable for mobile settings. In addition, maintenance-free, fixed optics should easily overcome the obstacles that crippled previous PMT instruments. The availability of a mobile instrument will greatly improve pollution monitoring capabilities and hazardous waste screening at onsite locations, thereby minimizing turnaround time. Additionally, trace metal analysis by DCP is currently an EPA-approved method, making analysis available for use by environmental laboratories and consultants performing waste remediation.[7] This is an important benefit, as EPA has been slow to approve and incorporate new analytical methods and technologies.

Acknowledgments

The authors gratefully acknowledge Pima County Wastewater Management for their assistance in addressing a need for an alternative method of analysis. It is hoped that continued research in this area will benefit municipal treatment facilities everywhere.

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QUALITY CONTROL FOR ELEMENTAL SPECIATION: MONITORING SPECIES TRANSFORMATIONS

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Abstract
An additional source of bias in elemental speciation compared to total elemental analysis is the species transformation, which is due to the instability of elemental species. Speciation transformation could either positively or negatively bias the analytical results, depending on the species' chemistry and the analytical procedures. As the stability of elemental species strongly depends on the sample matrix, and the species transformation may be kinetically controlled, the conventional quality control criteria may not be sufficient to validate an analytical procedure. This paper uses the analysis of Cr(VI) in soil to illustrate the importance of monitoring species transformation in elemental speciation.

The toxicity of an element highly depends on its chemical forms. For example, Cr(VI) is a carcinogen; Cr(III) at trace level is essential for human health. Therefore, the quantification of elements in their specific chemical forms, elemental speciation, provides more relevant information in environmental protection and remediation. There are only a limited number of available reference methods for elemental speciation. SW-846 Method 3060A is developed for analyzing Cr(VI) in soils. In SW-846 Update IV, Method 6800 describes an isotope dilution technique for elemental speciation, and is illustrated by the simultaneous determination of Cr(VI) and Cr(III) in aqueous samples or soil extracts using LC-ICP-MS. This paper will address some Quality Control (QC) issues regarding elemental speciation using the speciation of Cr(VI) and Cr(III) as an example.

In elemental analysis, in addition to the accurate control of the experimental conditions, quality control samples are prepared and analyzed along with the samples to ensure the quality of analytical results. These QC samples usually include method blank, method duplicate, matrix spike, and laboratory control samples (LCS), etc. The QC samples are used for two purposes: the control of experimental conditions and the evaluation of the matrix effects on the determination. While the experimental conditions can be evaluated by the analysis of the laboratory control samples, the use of matrix spike implies that it is not expected that the matrix of the laboratory control sample can exactly match that of the sample. In elemental analysis, matrix components may cause the loss of analytes during sample preparation and cause the sensitivity change during detection, etc. Dilution and method of standard addition are usually used to eliminate or compensate for such matrix effects.

There is one more factor that must be considered in elemental speciation, species transformation. For example, the interconversions between Cr(III) and Cr(VI) may occur under different pH/Eh. For the quantification of Cr(VI) in soil, the oxidation of Cr(III) causes a positive error; the reduction of Cr(VI) causes a negative error. The worst case might be that Cr(III) and Cr(VI) might transform bi-directionally, leading to an apparent satisfactory recovery for both Cr(III) and Cr(VI).

The current reference method (Method 3060A/7196A) for the quantification of Cr(VI) in soils involves the alkaline extraction (pH > 12) of water-soluble and water-insoluble Cr(VI) compounds, followed by neutralization (pH ~7.5) and colorimetric detection (pH < 2). Because of the great change of pH in this analytical procedure, there is a concern about the bi-directional transformations between Cr(III) and Cr(VI). Indeed, extensive researches have

been conducted to evaluate and minimize the species transformation during the method development stage.

Despite the great efforts that have been made to improve the determination of Cr(VI) in soils, the species transformations between Cr(III) and Cr(VI) are not completely evaluated following the current procedure. First, because a Cr(III) spike is not used, the possible oxidation of Cr(III) to Cr(VI) is not evaluated. This is simply due to the fact that both soluble and insoluble Cr(III) are not a representative of Cr(III) in sample. Thus, the observed oxidation of soluble Cr(III) does not mean that sample Cr(III) is oxidized; on the other hand, the observed non-oxidation of insoluble Cr(III) does not mean that sample Cr(III) is not oxidized. Consequently, using either soluble Cr(III) or insoluble Cr(III) as a quality control sample provides no useful information for evaluating the oxidation of sample Cr(III) to Cr(VI). Instead, the analyst has to rely on the faith that the addition of $MgCl_2$ inhibits such oxidation and that the oxidation of Cr(III) is unlikely to occur for Cr(III) existing in environmental samples. Second, since the observed low recoveries of Cr(VI) are usually due to the chemical reactions between Cr(VI) and the reducing matrix components rather than a relatively simple physical effect, one may not expect to get constant percent recoveries for both sample and its matrix spike. In other words, elemental species may undergo different degrees of the transformations between a sample and its matrix spike because they are actually two different samples. Therefore, the recovery of the matrix spike may not be a representative of that of the sample. Some experiments showed that the recovery of Cr(VI) depends on the amount of the Cr(VI) added into the sample matrix. More Cr(VI) was used, higher recovery of Cr(VI) was observed. This is understandable if we consider the concept of reducing capacity of a sample. One parameter of an environmental sample is the Chemical Oxidation Demand, which can be determined by the titration of a sample with $K_2Cr_2O_7$. If the total amount of titrant Cr(VI) is lower than a certain number, all Cr(VI) may be reduced; additional Cr(VI), however, will not be reduced. Thus, the recovery of Cr(VI) depends on the amount of Cr(VI) added. The dependency of the recovery on the amount of added Cr(VI) eliminates the possibility of using Method of Standard Addition (MSA) to ultimately improve the accuracy of determination. Third, the acceptable overall recovery for a species does not necessarily imply that they are static during an analytical procedure. Because of the possible bi-directional species transformations, positive error and negative error may cancel each other. Consequently, the overall recovery may appear to be satisfactory. For example, it has been observed that soluble Cr(III) can be oxidized during alkaline extraction; the loss of Cr(VI) may occur during subsequent neutralization and detection.

Speciated isotope dilution mass spectrometry (SIDMS), based on which Method 6800 is developed for elemental speciation, provides a more accurate and sophisticated elemental speciation method. Briefly, SIDMS uses the concept of spiking a sample with isotope-enriched materials. A spike with a unique isotope-enrichment is prepared for each species. For example, for the simultaneous determination of Cr(VI) and Cr(III) in water, two spikes are prepared: ^{50}Cr(III) is ^{50}Cr-enriched and is in Cr(III) form; ^{53}Cr(VI) is ^{53}Cr-enriched and is in Cr(VI) form. When these two spikes are mixed with a water sample, the sample Cr(III) and Cr(VI) are “labeled” with enriched isotopes. By measuring the altered isotope ratios in each of Cr(III) and Cr(VI) using LC-ICP-MS, the concentrations of Cr(III) and Cr(VI) in the original sample and any species transformations that occur after spiking can be quantitatively determined.

SIDMS uses isotope-enriched standards for two purposes: an internal standard for quantification and an isotope tracer for monitoring species transformations. SIDMS spikes **each** sample in an analytical procedure, so it monitors species transformations in each of the samples rather than in a separate sample per preparation batch or per group sample with the similar matrix. Thus, SIDMS provides more accurate species transformation information for each sample. In addition, because the spike recovery is determined by using an isotope in the **same** sample, it can be used to correct for the concentration of the species of interest. This is different from Method of Standard Addition in that in MSA, the recovery of an analyte is determined in another measurement. Unfortunately, species may undergo different degrees of transformation in two separate measurements, and the recovery may depend on the amount of the added spikes. Third, because SIDMS quantitatively monitors bi-directional species transformations, it can tell whether an apparent satisfactory recovery of a species is actually due to the cancellation of positive error and negative error in an analytical procedure.

Method 3060A/7196A provides an extensive discussion of the QC acceptance criteria, an indication of the importance of quality control issue in elemental speciation. In our opinion, more QC samples specific for monitoring species transformation may be required in these more conventional speciation methods. On the other hand, because the quantification of speciation transformation is already an integrated part of quantification in SIDMS, QC samples addressing species transformations maybe unnecessary.

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ION CHROMATOGRAPHY FOR THE 21ST CENTURY - RECENT DEVELOPMENTS FOR THE DETERMINATION OF INORGANIC ANIONS

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ABSTRACT
The new IonPac AS14A column provides similar performance to the existing AS14 column with increased peak efficiency and better pH stability. This column is also available in a 3 mm ID format which provides comparable run time to the AS4A column with better overall peak selectivity, significantly improved separation of fluoride from the column void volume and complete resolution of fluoride and small organic acids. While most anion exchange columns utilize carbonate-based eluents, the use of a potassium hydroxide eluent with an IonPac AS17 column represents an alternative approach to anion analysis which provides improved linearity and lower detection limits.

INTRODUCTION
U.S. EPA Method 9056a specifies the use of ion chromatography with an AS4A-SC anion separator column, a carbonate/bicarbonate eluent and chemically suppressed conductivity detection for the determination of inorganic anions in environmental waters and collection solutions from the bomb combustion of solid waste samples[1]. Both EPA Methods 9056a and 300.0, the comparable Office of Water method, allow the use of an optional column, provided that equivalent performance can be demonstrated[2]. Despite the fact that IC now is a mature analytical technique, considerable progress continues to be made in separator column, suppressor, and instrument development.

This paper will detail the different approaches employed in the production of anion exchange columns and review the performance of existing columns that are typically used with carbonate/bicarbonate eluents. The characteristics of a new column, the IonPac AS14A column, and its application to the determination of inorganic anions in environmental waters will be described.

While the majority of anion exchange columns used in IC today are developed for use with carbonate/bicarbonate eluents, hydroxide eluents offer the potential to improve linearity and lower Method Detection Limits (MDLs). However, this approach has not typically been used for the routine analysis of inorganic anions due to the lack of an appropriate hydroxide selective column and the difficulty in preparing contaminant free hydroxide eluents. In this paper, we also describe an alternative approach for the determination of inorganic anions in environmental matrices, based upon the use of automated eluent generation combined with a new hydroxide selective column, the IonPac AS17. The linear range, MDLs, potential interferences and application of this approach to a variety of environmental waters will be discussed.

EXPERIMENTAL

Instrumentation

Both DX-120 and DX-500 ion chromatographs (Dionex Corporation, Sunnyvale, CA) were used for this work. The DX-120 is a dedicated IC; the DX-500 is a modular IC system, which consisted of a GP50 Gradient Pump, an AS50 Automated Sampler, CD20 Conductivity Detector and LC20 Chromatography Enclosure. Dionex IonPac® AS4A-SC, AS14, AS9-HC, AS14A, and AS17 analytical columns and their respective guard columns, AG4A-SC, AG14, AG9-HC, AG14A, and AG17, were used for all separations. An EG40 Eluent Generator with an EluGen OH cartridge was used in conjunction with the AS17 column. Chemical suppression was achieved using a Dionex ASRS®-ULTRA. A Dionex PeakNet Chromatography Workstation was used for system control and data collection.

Reagents and Procedures

All solutions were prepared from analytical reagent grade chemicals in 18 Megaohm water, obtained from a Water Pro PS purification system (Labconco, Kansas City, MO). Stock solutions (1000 µg/mL) of fluoride, chloride, sulfate, nitrite, bromide, nitrate, and phosphate were prepared from their analytical reagent grade sodium salts (EM Science, Gibbstown, NJ). Stock standards were stored at 4°C and were all stable for at least one month. Working standards were prepared fresh daily. Commercially available (Dionex) eluent concentrates were used to prepare the eluents employed with the AS4A-SC, AS14, AS9-HC and AS14A columns.

All water samples were filtered through 0.45 µm syringe filters (Gelman, Ann Arbor, MI) prior to injection, with the exception of the domestic wastewater sample, which was passed through a preconditioned C_{18} Sep-Pak cartridge (Waters Corporation, Milford, MA) then filtered before injection. The soil sample was prepared by placing 10 g of dried soil in a 250 mL beaker and adding 18 Megaohm water to a total volume of 100 mL. The sample was extracted for 30 min in an ultrasonic bath, allowed to settle and filtered through a 0.45 µm syringe filter before injection.

RESULTS AND DISCUSSION

U.S. EPA Method 9056a specifies the use of an IonPac AS4A-SC anion exchange column with an eluent of 1.8 mM sodium carbonate/1.7 mM sodium bicarbonate for the separation of common anions. The method specifies the use of an AMMS® (Anion MicroMembrane Suppressor) operated in the chemical regeneration mode or an ASRS (Anion Self-Regenerating Suppressor) which provides equivalent method performance with added convenience. Conductivity is used as a bulk property detector for the measurement of inorganic anions.

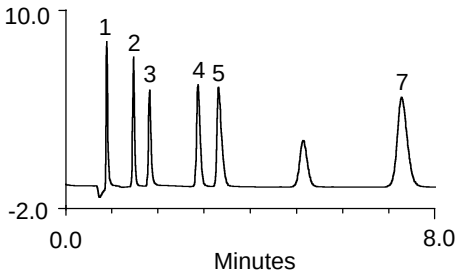


Figure 1. Separation of low-ppm anion standard using EPA Method 9056a. Conditions: column, Dionex IonPac AS4A-SC; eluent, 1.8 mM sodium carbonate / 1.7 mM sodium bicarbonate; flow-rate, 2.0 mL/min; detection, suppressed conductivity with an ASRS operated at 50 mA in recycle mode; injection volume, 50 µL; solutes, 1 - fluoride (2 mg/L), 2 - chloride (3 mg/L), 3 - nitrite (5 mg/L), 4 - bromide (10 mg/L), 5 - nitrate (10 mg/L), 6 - phosphate (15 mg/L), 7 - sulfate (15 mg/L).

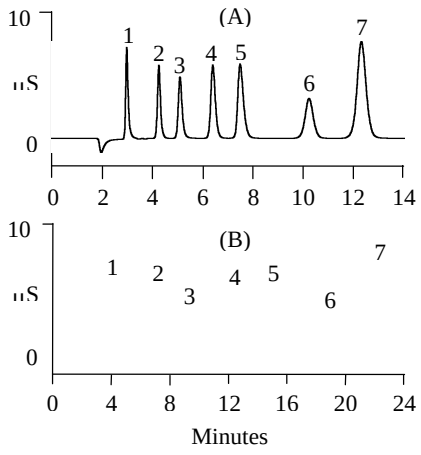
Figure 1 shows a typical chromatogram of a standard containing low-ppm levels of inorganic anions separated using an IonPac AS4A-SC column. The AS4A-SC resin is a pellicular, latex agglomerated material with a substrate of ethylvinylbenzene (EVB) crosslinked with 55% divinylbenzene (DVB), which makes the column 100% solvent-compatible. All the anions are well-resolved within a total run time of less than 8 min. The linear coefficients of determination (r^2), calculated MDLs, and retention time and peak area precision (expressed as % RSD) which can be achieved for each of the anions using the AS4A-SC column are shown in Table I.

The selectivity of the AS4A-SC column is essentially the same as the original AS4A column, which was developed in the early 1980's. In general, the selectivity of the AS4A-SC permits acceptable recoveries to be obtained for common anions spiked into environmental water matrices. However, the determination of fluoride at concentrations less than 1.5 mg/L is subject to interference from mg/L levels of small organic acids, such as formate and acetate, when using the AS4A column. Consequently, this column is not recommended for the analysis of fluoride in complex samples which contain small organic acids, such as domestic wastewaters or solid waste leachates where acetate is used for pH adjustment[1].

Table I. Linearity, MDLs, retention time and peak area precision obtained for inorganic anions using Method 9056a with an IonPac AS4A-SC column and a 50 mL injection.

Anion	Range (mg/L)	Linearity (r^2)	Calculated MDL (µg/L)	Peak Rt precision	Peak Area precision
Fluoride	0.1 - 100	0.9971	5.9	0.48%	0.67%
Chloride	0.2 - 200	0.9996	2.3	0.30%	0.47%
Nitrite-N	0.1 - 100	0.9997	1.8 (5.7 as NO_2)	< 0.05%	0.53%
Bromide	0.1 - 100	0.9967	9.7	< 0.05%	0.13%
Nitrate-N	0.1 - 100	0.9969	1.4 (6.2 as NO_3)	0.40%	0.17%
o-Phosphate-P	0.1 - 100	0.9967	5.8 (17.8 as PO_4)	0.30%	0.35%
Sulfate	0.2 - 200	0.9975	6.7	< 0.05%	0.14%

Both Methods 9056a and 300.0(A) allow the use of alternative anion exchange columns, provided that equivalent method performance can be demonstrated. Figure 2 shows chromatograms obtained using two more recent alternative columns for anion analysis: the AS14 column (A) and AS9-HC column (B).



The IonPac AS14 column (A) is packed with a macroporous resin of EVB crosslinked with 55% DVB that has a methacrylate-based functional group grafted onto the surface. The AS14 column provides complete resolution of fluoride from small organic acids, in addition to improved separation of fluoride from the void peak. The improved selectivity and higher capacity of the AS14 column (65 µeq compared to 20 µeq for the AS4A-SC) allows quantitative recoveries to be obtained for common anions spiked into environmental waters, including complex matrices such as domestic wastewaters, aqueous soil extracts, or solid waste leachates.

Figure 2. Separation of low-ppm anion standard on Dionex IonPac AS14 and AS9-HC columns. Conditions: as for Figure 1, except; columns, (A) AS14 and (B) AS9-HC; eluents, (A) 3.5 mM sodium carbonate / 1.0 mM sodium bicarbonate and (B) 9.0 mM sodium bicarbonate; flow-rates, (A) 1.2 mL/min and (B) 1.0 mL/min.

While the AS14 column provides suitable performance for the determination of anions in the majority of wastewater samples, very high ionic strength samples are best analyzed using a higher capacity column, such as the IonPac AS9-HC column (B). This column uses a macroporous (2000 Å pore size) resin consisting of EVB crosslinked with 55% DVB. This core particle allows the methacrylate-based latex layer to be thinly coated on both the exterior and interior surfaces of the resin and provides a simple way to produce a column with higher capacity (190 µeq). This column is recommended for the analysis of high ionic strength samples, e.g., the determination of sub-ppm levels of nitrite in wastewater containing high levels of chloride. When using suppressed conductivity detection, a maximum chloride/nitrite ratio of 10,000:1 can be analyzed on this column. Better performance is obtained with direct UV detection, and a maximum chloride/nitrite ratio of 100,000:1 can be analyzed using this approach. The high capacity AS9-HC column is specified in EPA Method 317.0 for the analysis of disinfection by-product anions, while a similar macroporous resin was used to produce the IonPac AS16 column, which is specified in EPA Method 314.0 for the analysis of perchlorate by IC.

Dionex recently introduced a new anion exchange column, the IonPac AS14A, which is intended as an alternative to the three columns described above for the analysis of common anions. The IonPac AS14A column was designed to have similar selectivity to the AS14, but with higher capacity, improved peak shape, and better chemical stability. The AS14A column is available in two formats; 150 x 3 mm ID (5.5 µm diameter particle) and 250 x 4 mm ID (7.0 µm diameter particle). The 250 x 4 mm ID AS14A has similar selectivity compared to the AS14 column, although the higher capacity AS14A (120 µeq/column) uses a higher ionic strength eluent in order to achieve similar retention times. The novel block-grafting technique used to produce the AS14A column

produces a more uniform functionalized layer on the column surface, resulting in improved peak efficiencies. Figure 3 shows a chromatogram of a low-ppm level anion standard obtained by using the AS14A column (3 mm ID format). This new column provides similar overall run times and peak response compared to the AS4A-SC column, but with significantly improved separation of fluoride from the column void volume, complete resolution of fluoride and acetate, in addition to better overall peak selectivity. The linear coefficients of determination (r^2), MDLs, and retention time and area precision (expressed as % RSD) which can be achieved using the IonPac AS14A column are shown in Table II.

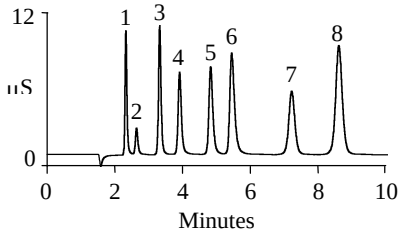


Figure 3. Separation of low-ppm anion standard on a Dionex IonPac AS14A column. Conditions: as for Figure 1, except; column, AS14A (150 x 3 mm ID); eluent, 8.0 mM sodium carbonate / 1.0 mM sodium bicarbonate; flow-rate, 0.5 mL/min; injection volume, 25 µL; solutes, 1 - fluoride (1 mg/L), 2 - acetate (4 mg/L), 3 - chloride (2 mg/L), 4 - nitrite (3 mg/L), 5 - bromide (5 mg/L), 6 - nitrate (5 mg/L), 7 - phosphate (8 mg/L), 8 - sulfate (6 mg/L).

The new IonPac AS14A column (in 3 mm ID format) provides comparable run time to the AS4A column with better overall peak selectivity, significantly improved separation of fluoride from the column void volume, and complete resolution of fluoride and acetate. The 3 mm ID format would be a suitable column to substitute in place of either the AS4A or AS14 columns for the analysis of anions in moderate ionic strength environmental waters. While the AS14A column represents the latest example of a carbonate-selective, anion exchange column, an alternative approach for the determination of inorganic anions is to use hydroxide as the eluent. Hydroxide eluents have not typically been used for the routine analysis of common inorganic anions due to the lack of an appropriate hydroxide selective column and the difficulty in preparing contaminant-free hydroxide eluents.

Table II. Linearity, MDLs, retention time and peak area precision obtained for inorganic anions using the IonPac AS14A (150 x 3 mm ID) column and a 25 µL injection.

Anion	Range (mg/L)	Linearity (r^2)	Calculated MDL (µg/L)	Peak Rt precision	Peak Area precision
Fluoride	0.1 - 100	0.9983	3.1	0.16%	0.35%
Chloride	0.2 - 200	0.9996	5.4	0.12%	0.14%
Nitrite-N	0.1 - 100	0.9999	1.8 (5.7 as NO_2)	0.12%	0.39%
Bromide	0.1 - 100	0.9979	8.9	0.15%	0.44%
Nitrate-N	0.1 - 100	0.9979	1.7 (7.7 as NO_3)	0.15%	0.37%
o-Phosphate-P	0.1 - 100	0.9981	5.1 (15.6 as PO_4)	0.10%	0.42%
Sulfate	0.2 - 200	0.9988	9.6	0.10%	0.21%

The use of an Eluent Generator (EG40), a device which produces high purity hydroxide eluents for IC by electrolysis of DI water, combined with a new hydroxide-selective, anion exchange column, the IonPac AS17, represents a totally new approach to the determination of anions in environmental waters. Figure 4 shows an example of the resolving power which can be achieved using the AS17 column, an electrolytically generated hydroxide gradient and suppressed conductivity detection. Fluoride, acetate, propionate, and formate are completely resolved, while other potential interferences, such as oxyhalide anions (chlorite, bromate, and chlorate) and oxalate, are also resolved from the common inorganic anions under these conditions.

In addition to eliminating the need to manually prepare eluents, the EG40 offers the added benefit of producing carbonate-free hydroxide eluents on-line. As there is essentially no carbonate contamination, minimal baseline shift is seen during the gradient separation when using this automated eluent generator, as evident in Figure 4. The linearity (r^2), MDLs, and retention time and area precision (% RSD) which can be achieved using the AS17 column and automated eluent generation are shown in Table III.

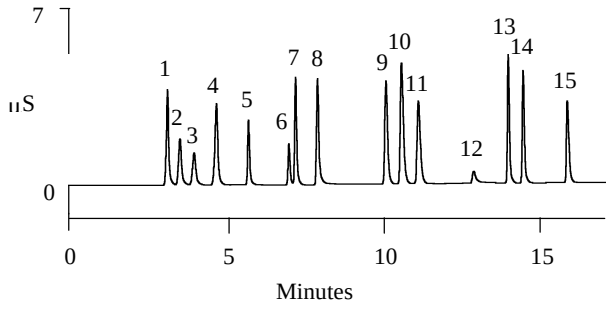


Figure 4. Separation of an expanded anion standard on a Dionex IonPac AS17 column. Conditions: as for Figure 3, except; column, AS17; eluent, 1 – 35 mM potassium hydroxide gradient generated with an EG40; flow-rate, 1.5 mL/min; solutes, 1 - fluoride (2 mg/L), 2 - acetate (5 mg/L), 3 - propionate (5 mg/L), 4 - formate (5 mg/L), 5 - chlorite (5 mg/L), 6 - bromate (5 mg/L), 7 - chloride (3 mg/L), 8 - nitrite (5 mg/L), 9 - bromide (10 mg/L), 10 - nitrate (10 mg/L), 11 - chlorate (10 mg/L), 12 - carbonate, 13 - sulfate (15 mg/L), 14 - oxalate (5 mg/L), 15 - phosphate (15 mg/L).

Table III. Linearity, MDLs, retention time and peak area precision obtained for inorganic anions using the IonPac AS17 column and a 25 µL injection.

Anion	Range (mg/L)	Linearity (r^2)	Calculated MDL (µg/L)	Peak Rt precision	Peak Area precision
Fluoride	0.1 - 100	0.9996	2.9	0.21%	0.18%
Chloride	0.2 - 200	0.9999	2.6	< 0.05%	0.13%
Nitrite-N	0.1 - 100	0.9982	1.0 (3.2 as NO_2)	< 0.05%	0.26%
Bromide	0.1 - 100	0.9993	6.8	0.09%	0.23%
Nitrate-N	0.1 - 100	0.9999	1.0 (4.2 as NO_3)	< 0.05%	0.19%
o-Phosphate-P	0.1 - 100	0.9999	4.0 (12.3 as PO_4)	< 0.05%	0.40%
Sulfate	0.2 - 200	0.9999	5.2	0.07%	0.23%

A comparison of the data above in Table III with that shown previously in Table I demonstrates the advantages of using hydroxide eluents. Linearity was improved, with correlation coefficients (r^2) of >0.998 over a three decade concentration range; MDLs were approximately 50% lower, despite using a smaller (25 µL) injection volume; retention time precision was <0.25% RSD, and peak area precision was <0.5% RSD. The use of the EG40 further enhances method performance by increasing the automation of the instrument. No solution other than water is required to operate the system for routine analysis, as the EG40 electrolytically generates the hydroxide eluent, while the ASRS device electrolytically generates the acid used for the suppression reaction.

SUMMARY

Considerable progress has been made in IC column development in recent years. The new IonPac AS14A column (in 4 mm ID format) provides similar performance to the existing AS14 column with increased peak efficiency, better pH stability and higher column capacity. The 3 mm ID format provides comparable run time to the AS4A column with better overall peak selectivity, significantly improved separation of fluoride from the column void volume and complete resolution of fluoride and acetate. The use of IC with an IonPac AS17 column, EG40 Eluent Generator and potassium hydroxide gradient represents a new approach to the determination of inorganic anions in environmental waters. This approach is a modification of U.S. EPA Method 300.0, which allows equivalent method performance with improved linearity, precision, and MDLs, in addition to increasing the level of automation of the IC system.

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FIELD DEMONSTRATION PROJECTS FOR THE EVALUATION OF ALTERNATIVE TECHNOLOGIES FOR PROVIDING CONTINUOUS MONITORING OF NITROGEN AND PHOSPHORUS IN FRESH WATER STREAMS

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ABSTRACT
The National Institute for Environmental Renewal (NIER) is assessing the ability of new technologies to provide continuous measurements of nutrients in the nontidal regions of the Chesapeake Bay Watershed. A four-step process to identify and evaluate alternative technologies was developed and implemented. First, based upon published literature and vendor supplied information, candidate technologies were screened against the requirements of monitoring programs. This resulted in a short list of flow injection technologies that can monitor ammonia, nitrate and orthophosphate on a continuous base. Second, a short-term field demonstration to provide an initial shakedown, develop the calibration and maintenance requirements, and integrate into data acquisition platform was designed. Third, long-term field demonstration in partnership with an ongoing monitoring program will be conducted. This will provide a comparative analysis with traditional monitoring procedures. Fourth, recommendations for integrating alternative technologies into ongoing monitoring programs will be made.

INTRODUCTION
The National Institute for Environmental Renewal (NIER) is assessing the ability of new technologies to provide continuous measurements of nutrients in the nontidal regions of the Chesapeake Bay Watershed. While water quality monitoring is conducted by dozens of federal, state, local, and private organizations in order to meet numerous data requirements, there are many common requirements in the areas of parameters, sampling, analysis procedures, QA/QC requirements, etc. Specifically, there is a high level of interest in the management of nutrients (nitrogen and phosphorous) and sediments within the watershed. This results in the need to quantify surface water contaminant concentration and concentration variability. This paper summarizes activities conducted to date in field testing and validating alternative technologies for measuring nutrients in streams.

For the purposes of this paper, alternative technologies are defined as any technology that is not currently being routinely used for water quality analysis. Alternative technologies may include new sensor types or incorporation of existing sensor technologies into a data collection/data management platform.

REQUIREMENTS FOR ALTERNATIVE TECHNOLOGIES
As the issues facing environmental managers become more complex, there is an increasing need for access to water quality monitoring data. In this area of limited resources there is a continuous need to find more cost effective methods for collecting and managing data. Several programs are attempting to address these needs. For example under Directive 98-3, the Executive Council of the Chesapeake Bay Program calls for the Bay Program to utilize new and innovative technologies to meet the goals and commitments of the Bay restoration. Many of these goals and commitments are associated with nutrient and sediment loads into, and ambient concentrations within the Bay.

As part of an overall review of water quality monitoring programs, NIER conducted a review of the requirements of the data users. This review included a survey of data users, a review of literature addressing data needs, and analysis of a compendium database of monitoring results compiled over a twenty-year period. We identified areas where alternative technologies may be appropriate (NIER, 1999a):

Near real time data reporting
There is a need for near real time reporting of water quality data. Data uses identified were public health (drinking water intakes and swimming), tracking of spills, using instantaneous water quality conditions as a basis for the initiation of more intensive sampling using traditional methods (conditional sampling), and providing the public with near real time information. A survey of data users showed that 10 to 20% of the federal state and local government agencies expressed a need for near real time reporting of ambient water quality data.

Continuous monitoring and near real time data reporting of flows and water levels are presently employed throughout the watershed. Data users include emergency response officials and water supply managers. These data are used to plan emergency response to floods and droughts and provide the public with up to date information.

Continuous monitoring

A literature review and a data users survey showed that sample collection frequencies of current monitoring programs typically monthly with some storm event sampling) were not short enough to quantify the variability of water quality. Specific areas where more frequent monitoring is required include:

- storm event monitoring,
- monitoring the effectiveness of Best Management Practices that have been implemented,
- quantification of nonpoint source loads of nutrients, and
- characterizing the quality the various flow regimes (groundwater inputs, snowmelt, etc.) that constitute streamflow

The data users survey showed that storm events, monthly, and seasonal collection were the most commonly needed. High frequency (continuous, daily, or weekly) data collection presently accounts for 5% of state, 10% of local and 20% of federal agency requirements.

The need for continuous monitoring of water quality is greater than that of near real time data reporting.

BARRIERS TO USE OF ALTERNATIVE TECHNOLOGIES

Although field portable instruments are routinely used for measuring pH, conductivity, turbidity, temperature, and dissolved oxygen, the data collected using these instruments are generally considered as “field data” and they have not been effectively incorporated into the monitoring programs in the watershed. Nitrogen and phosphorus species are almost never measured in the field. Numerous instruments have demonstrated performance in research applications; they have not been adopted in routine ambient water quality monitoring programs.

The major obstacles to routine use are unanswered questions concerning data quality, reliability, calibration and maintenance requirements, and costs. In addition, there is hesitancy with the monitoring community to adopt any new analytical methods. Any candidate technology must clearly demonstrate that it will produce results that are equivalent to (or at least comparable with) historical data prior to adoption. In order to address these issues, a four-step process was developed and implemented. The requirements of ongoing monitoring programs were synthesized into a set of performance criteria (NIER, 1999b). The criteria included detection limits, quantitation range, power requirements, environmental conditions, and maintenance intervals and were used to screen candidate technologies.

The technology evaluation four-step process includes:

1. Identification of candidate innovative technologies.
2. Short-term field demonstration to provide an initial shakedown, develop the calibration and maintenance requirements, and integrate the technology into a data acquisition platform.
3. Long-term field demonstration in partnership with an ongoing monitoring program. This will provide a year-long comparative analysis with traditional monitoring procedures.
4. Recommendations for integrating alternative technologies into ongoing monitoring programs.

STATE OF THE ART

An extensive review of published literature and vendor supplied information was conducted. The purpose of this review was to:

1. Identify technologies that had been developed to the point where they were ready for field testing,
2. Evaluate the performance of the instruments (quantitation range, accuracy and precision, calibration and maintenance requirements, reliability, etc.) against the requirements of the Chesapeake Bay monitoring programs, and
3. Recommend a short list of candidate technologies for field testing.

The review revealed that considerable progress has been made in the development of instrumentation for continuous monitoring. Instruments that have been developed in the areas of process control of water (Pollack et al., 1999) and wastewater treatment and oceanography appear to be well suited for freshwater applications. Of particular interest are instruments using flow injection technology to produce analogs to traditional wet chemical analysis for ammonia, nitrate, and phosphate.

Flow injection technologies have two general schemes for quantitation:

- ion selective electrode analysis and sample adjustment capabilities, and
- wet chemistry techniques for sample analysis (spectrophotometric/ colorimetric).

There are two major flow analysis approaches: flow injection (FIA) and continuous flow analysis (CFA) (Linares et al., 1992). The first flow injection analysis paper was published in 1975 by Ruzicka and Hansen. Since that time, FIA/CFA have become a routine laboratory technique for sample analysis and on-line sample treatment. These techniques offer fast response time (typically 10-120 seconds), high sample throughput (typically 30-120/h), low reagent consumption (typical flow rates are 0.5-2.0 mL/min), and are easily adapted to automated analysis.

Flow injection analysis and continuous flow analysis are very similar sample delivery systems for analytical measurement. Flow injection refers to the introduction of the sample into a measurement situation via an artificial delivery mechanism. The sample is extracted from its environment by a mechanical means and then is introduced into the analyzer and data is recorded at intervals prescribed by the operator.

Continuous flow refers to the sample delivery by a continuous flow feed line or stream of sample that enters the analyzer. The sample enters the analyzer via gravity feed or by mechanical delivery. An uninterrupted stream of sample flows through the system, the analytic concentrations are measured and the data is recorded. Data can be recorded on a continuum with a data logging system.

Normal FIA (n-FIA) involves the injection of a sample (injection stream) into an unsegmented continuously flowing reagent stream (carrier stream). In the reaction manifold the sample undergoes controlled physical dispersion and chemical reaction to form a detectable species. Once transported to the detector the analyte concentration can be measured (Blundell and Worsfold, 1995).

Basic components of a flow injection system are a pump to propel the sample, reagent stream(s), an injection valve, reaction manifold, and a flow-through detector. Detectors include but are not limited to UV/VIS spectro-photometers, light emitting diodes (LEDs), and ion selective electrodes (Blundell and Worsfold, 1995).

More recent applications of FIA/CFA focus on *in situ* monitoring of natural and polluted waters. These techniques offer continuous/near-continuous, quantitative data for a wide range of parameters including dissolved and total nitrogen and phosphorus species.

A variation on FIA, reverse FIA (r-FIA), has reportedly increased the sensitivity and reduced the reagent consumption in this type of analysis. Reverse FIA is suitable for applications in which sample is in abundant supply, as in the case of natural water monitoring (Andrew et al., 1994). The variation consists of injecting small volumes of reagent (injection stream) into the flowing sample stream (carrier stream), rather than the conventional injection of sample into a flowing reagent stream. Johnson and Petty have reported (in the determination of phosphate in seawater) that reversing the roles of the streams results in increasing the sensitivity by a factor of five (Johnson and Petty, 1983).

In general, information about the technologies was incomplete and inconsistent making a comparative analysis difficult. For example, authors reported a lower limit of detection or when a non-zero detection limit was reported the method of determination was not stated. However, several commercial products were identified that appear to meet the requirements of watershed monitoring programs. Table 1 presents the parameters, required detection range, and quantitation schemes of alternative technologies.

While the initial screening of technologies focused on each parameter, the most recent products can analyze for all three parameters. The final selection of product(s) for field testing will be made after cost and availability issues have been resolved.

Table 1. Alternative Technologies for Monitoring Nutrients		
Parameter	Required Range, mg/L	Quantititation Technologies
Ammonia	0.02 – 1.4	Ion selective electrode; Colorimetric (Nessler)
Nitrate	0.05 – 7.0	Ion selective electrode; Colorimetric(Cadmium Reduction)
Orthophosphate	0.01 – 0.4	Colorimetric

FIELD TESTING

The next step is field evaluation of candidate monitoring technologies. At this time, a workplan is being developed for the two field testing phases. The plan is based upon the performance specifications that have been developed.

Analytical Capabilities

- Ability to Measure Nutrient Parameters - Technologies must demonstrate the ability to measure flow in surface water:
  - Ammonia,
  - Nitrate, and
  - Dissolved Orthophosphate.
- Detection Limits – Detection limits must approximate EPA-approved standard reference methods for analyte specific parameters.
- Range of Detection – Technologies must be capable of measuring concentrations over the ranges typically found in historical data for the Chesapeake Bay Watershed.
- Accuracy and Precision - Accuracy and precision will be targeted at an expected standard recovery of 90-110%. The minimum requirements for accuracy and precision will be at least 80-120% recovery.
- Interferences – Technologies must not be subject to interference by any chemical/physical characteristic expected to be encountered in the nontidal regions of the Chesapeake Bay Watershed. Specifically, the technology must be able to perform in water quality environments that contain suspended sediment in concentrations up to 100 mg/L.

Instrumentation

- Operation – The instrument must be operable by a field technician after one day of training. Operation includes installation, calibration and data collection.
- Maintenance – Instruments must require minimal factory servicing within a 12 month period of operation. The manufacturer must have a service facility and a manufacturer's representative in the United States.
- Operating Environment – Instrument durability and construction materials will be evaluated in consideration of the field environments proposed for instrument use. The instruments must be weatherproof and operational in temperatures above freezing. Instruments must be able to operate in depths to 10 meters.
- Power Requirements – Technologies must meet standard power requirements (adaptable to the field data acquisition system) to be included in the field demonstration.

Data Acquisition

- Period of Time Required for Reporting - An instrument/technology must have the ability to transfer data to a data logger in a timely fashion.
- Costs (Initial and Operational) - Initial instrument/technology acquisition and maintenance and materials costs will be reviewed and must not be prohibitively expensive relative to the information they can provide.
- Calibration - Technologies will have the ability to be calibrated to 2 points at a minimum and maintain calibration for a minimum of one week. The instruments must also be capable of field calibration.
- Data Acquisition Signal/Response – The serial communications must be capable of identifying the following signal types: RS232, FSK modulated (RF modem), RS485, or TTL.
- Sampling/Analysis Frequency - Instruments must be capable of performing analyses in short time intervals and be capable of sampling frequency alteration based on changes in field events. Sampling and analysis frequency will be targeted at 5 minutes, but at a minimum, 15 minute sampling analysis intervals will be accepted.

The design of the field testing system is complete. Data will be collected using a data collection platform capable of transfering data on a real-time or near real-time basis. Alternative technologies will be deployed along with water quality monitoring sensors that have been routinely used in water quality studies for their value as "water quality indicators." These parameters will include turbidity, conductivity, pH and depth. The information collected by the water quality sondes will be used for supplemental water quality data and for data comparison purposes in the new technology evaluation process. Some of the applications are as follows:

- Turbidity can be correlated to the amount of sediment suspended in a stream.
- Conductivity is dependent on ion presence and the ability to carry an electrical current; this information can be used to estimate ion mobility in a stream.
- pH is used to indicate changes in acid/base chemistry of the stream.
- Depth measurements, when used in conjunction with a stage/rating curve, are used to calculate stream discharge. This information is required for calculation of loads and for analysis of the relationship between water quality and flow regime.

These technologies utilize existing, proven methods of analyses that include nephelometry for turbidity, alternating electrical current/electrode measurement for conductivity, ion selective electrode measurement for pH and pressure transduction for depth.

Meteorological data that may be useful in modeling, estimating increases in stream flow and predicting or understanding the changes in the rate of transport of pollutants in a stream will also be collected. Meteorological monitoring will include rainfall, wind speed and direction, humidity, barometric pressure, and temperature. Barometric pressure is necessary for atmospheric correction of depth measurements from unvented pressure tranducers.

A fixed field station (containing power, data logging, and communications equipment) has been constructed at the NIER laboratory adjacent to the Lackawanna River in Mayfield, Pennsylvania. This will be used for the short term field evaluation phase. For the long term phase, a mobile station will be constructed and located at a permanent water quality monitoring station. The final work plan will specify procedures for determining the costs, operating and maintenance requirements, and quality of data (precision, accuracy, and comparability) of the alternative technology.

SUMMARY

High frequency measurement of nutrients in surface water and, in some cases, rapid reporting of results are required to meet management objectives of many monitoring programs within the Chesapeake Bay watershed. Commercially available field instruments that couple flow injection and wet chemistry or spectrophotometric analytical techniques appear to meet the data criteria of the monitoring programs. A testing protocol for the field instrumentation has been developed.

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MINIMIZING THE CONTAMINANT CHARGE FOR INDUSTRIAL EFFLUENT

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The present research was performed in a chemical industry of synthesis from the region of Orizaba. The main and final goals were to minimize the contaminant charge applying a physicochemical treatment and to make a proposal for treatment of the industrial effluent.

During the sampling and characterization periods of industrial wastewaters in the place where the research was performed there were observed three different types of discharging waters. Water from where the discharging flux sanitary wastewater was negligible compared with the ones from the process or the washing of containers. This was the reason it was decided not to include it on the characterization and the subsequent treatment.

A variety of high concentrations of BOD, COD, pH, suspended solids, etc. was found due to the intermittent nature of the process. As such it became essential to stabilize a physicochemical treatment in order to define the procedure, dose and appropriate chemicals for this type of waters.

In order to determine the technical feasibility of the physicochemical treatment, fourchemicals were tested: C-4200, A-900, C-2012 and aluminum sulphate. The results were satisfactory along the preliminary trials and the flocculate formation and the clarification. The chemicals used were aluminum sulphate and C-2012 on the range of 100 - 500 ppm.

While the optimization of the treatment was in process the results with aluminum sulphate were not the best, and this was the reason we tried other chemicals. A systematized process was established and the results showed an acceptable effectiveness on the removals: BOD, 75-93 %; COD, 37-87 %; suspended solids, 40 - 100 % and turbidity 75 - 99 %. Tthe recommended doses are 500 ppm C-2012 and 0.025 g/l of BA-01. The speed and the stirring time recommended are: stirring fast 100 rpm, 2 min, mixing of flocculation 45 rpm, 3 min; stirring slow 26 rpm, 5 min.

According to the previous results the water treatment plant should have a pretreatment including the conduction of raw water though the stainless steel tubing of one inch diameter wide with 0.5 x 0.5 cm opening strainer for solids retention homogenization pool. Following the pretreatment should have been the pumping of the homogenized volume to the physicochemical treatment to perform the flocculation-coagulation. Next, should have later been the decantation where the sludge should have been separated from the treated water for its latter disposal. Finally the treated water should have to be thrown to the receptor body through the channel passing previously through a Parshall gauger in order to control the volumen's effluent.

THE CHEMISTRY OF TCLP TESTING OF FLUORESCENT LAMPS

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In the course of developing a protocol for fluorescent lamp TCLP testing, it was discovered that some variation in test results can occur irrespective of controlled test conditions. Some causes for variation are conditions under which the test is performed, unique lamp structure, and chemical reactions that are not at equilibrium after the prescribed test time. Test conditions, lamp structure, and chemical factors that affect fluorescent lamp TCLP test results will be described. An understanding of these factors has been critical to the development of TCLP compliant fluorescent products.

YOUR CONTRIBUTION TO THE CO_2 BUILDUP IN THE ATMOSPHERE

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INTRODUCTION

It is customary to speak of global carbon budgets in gigatons or other large measures. How much do we, as individuals, contribute to the rising concentration of CO_2 in the atmosphere? This poster will present data on the annual CO_2 output of one person and one car, and the approximate area of various forests required to absorb this CO_2 by photosynthesis.

The average person exhales 445 liters of CO_2 per day[1] which is roughly 700 pounds/year. That is dwarfed by the CO_2 production of the average car that uses 552 gallons of gasoline/year[2], producing roughly 10,000 pounds (5 tons) of CO_2. For the purpose of this presentation we will consider the areas of various forests required to absorb 5 tons of CO_2/year.

Nature's response to the CO_2 buildup is the process of photosynthesis which absorbs CO_2. Lawns contribute to this process but do not serve as a permanent repository because they are mineralized in a relatively short period of time. Forests are a more permanent repository of carbon, therefore they will be the focus here.

NET PRIMARY PRODUCTIVITY

The actual storage potential of CO_2 is determined by the photosynthetic rate of a given system minus its respiration rate. Trees absorb CO_2 but they also emit a portion of it in respiration. Roots of trees and growing plants emit CO_2, as do microbes in the soil. Therefore, in assessing the potential of a forest to absorb CO_2 it is necessary to measure both the CO_2 absorbed by the system and how much it emits over a long period of time. An alternate approach is to measure gains in the size of trees and their roots, and make measurements of soil emission rates. These are difficult and time-consuming tasks but they provide a measure of the net primary productivity (NPP).

The data shown in the ensuing sections represent estimates of the area requirements for various forests to absorb 5 tons of CO_2/year. Obviously, variables such as rainfall, latitude, and temperature would influence the performance of each forest.

FOSSIL FUEL EMISSIONS IN PERSPECTIVE

The focus of this presentation is on one's personal contribution to the atmospheric buildup of CO_2 by driving a car. At the same time, mention should be made of the buildup of CO_2 relative to other processes.