EPA'S ENVIRONMENTAL MONITORING RESEARCH PROGRAM SESSION (Continued)

QUALITY ASSURANCE

GENERAL

was tested for mechanical ruggedness and its ability to collect subsurface bound organics. The vertical profile of two borings are shown in Table 3. PAHs were found at depths of 97-cm and 142-cm at boring one and 130-cm. The hot organic vapor was cooled by dry ice and collected in an empty glass sleeve attached to the transfer line. Total collection and analysis time required at each depth location was approximately 15-min per sample inclusive of sample collection, transfer line back flushing, and analysis time. Unfortunately, comparison measurements between the TECP measured concentrations and actual soils collected at depth and analyzed by standard GC/MS methods were not possible since ARA was unable to re-enter the hole with a soil sample collection probe without breaking the CP rod. The results produced to date are promising suggesting that direct on-line chemical measurements of subsurface contaminants may be possible within a couple years.

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AN INTEGRATED NEAR INFRARED SPECTROSCOPY SENSOR FOR *IN-SITU* ENVIRONMENTAL MONITORING

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The monitoring of environmental organic contaminants currently involves off-site methods which prohibit optimal usage. This study explores the possibility of combining the principles of interferometry with that of near infrared evanescent wave absorption spectroscopy to produce a novel integrated sensor technology capable of monitoring and determining *in-situ* the concentration of numerous organic analyte species simultaneously. This novel sensor promises to be non-intrusive and to provide accurate, rapid, and cost effective data. The overall instrument is envisioned to be compact, portable, rugged, and suitable for real time monitoring of organics. The sensor consists of a symmetric, single mode Mach-Zehnder interferometer with one arm (sampling) that is either exposed directly to the analyte or coated with a thin hydrophobic layer that enhances the binding of pollutant molecules onto its surface. A glass buffer layer protects the second arm (reference) from the influence of pollutants. Light is coupled into the waveguide and split between the sampling and reference arms using a Y-splitter configuration. Changes in the refractive index caused by the presence of organic contaminants result in a measurable phase difference between the sampling and reference arm. Selectivity of the sensor is achievable by utilizing evanescent wave absorption spectroscopy in the near infrared, a technique which measures wavelength dependent refractive index changes. The waveguide structures used in this study are fabricated on 10 cm silicon wafers. V-grooves are first formed in the silicon substrate to hold the fibers which couple to the ends of the Mach-Zehnder interferometer. A 10 μm thick SiO_2 film is synthesized by low pressure chemical vapor deposition (LPCVD) to act as cladding material for the waveguide and prevent light from coupling with the underlying silicon. A 4 μm thick phosphorus-doped (7.5 wt% P) LPCVD SiO_2 film is then deposited to act as core material for the waveguide. This layer is patterned using standard lithographic exposure and plasma etching techniques and subjected to a 1050 ºC anneal to cause viscous flow and round off the edges. This rounding-off procedure is necessary to minimize coupling losses between fiber and waveguide. The refractive index of the doped glass is near 1.48, thus, producing with the underlying SiO_2 (n=1.46) substrate a single mode waveguide device. Deposition of a 0.5 µm thick LPCVD undoped SiO_2 buffer layer over the entire wafer and a subsequent lithographic step results in selective removal of that layer over the sampling arm of the interferometer. This configuration allows for exposure of the sampling arm (uncoated or coated) to various contaminants in the environment which cause a change in the effective refractive index of that arm. The arm coated with the SiO_2 buffer layer sees a constant refractive index of n=1.46. A lithographic mask is used to produce the required patterns. Five micron wide waveguides form the two interferometer paths using a splitting angle of 2º. The sampling and reference arms are at a fixed separation of 50 µm and variable lengths (4, 6, 8, and 10 mm). A detailed analysis of these processing steps together with the principles of operation of the sensor will be discussed.

A NITRIC OXIDE AND AMMONIA SENSOR ARRAY FOR FOSSIL FUEL COMBUSTION CONTROL

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ABSTRACT

In fossil fuel combustion processes, nitric oxide (NO) emissions are minimized by a selective catalytic reduction (SCR) technique where ammonia (NH_3) is injected into the flue gas stream to react with NO to form environmentally safe gases such as nitrogen and water vapor. Unfortunately, this process is usually incomplete, resulting in either NO emissions or excess NH_3 (NH_3 slip). Therefore, a critical need exists for an *in situ* sensor array to continuously monitor the NO and NH_3 levels at the output of the SCR system near the stack to provide real time control of the NH_3 injection and hence minimize the NO emissions to the environment. Chemiresistive sensor technology is being used to develop a small, portable, sensitive and selective sensor array that has potential to continuously measure NO and NH3 emissions. The sensor array utilizes a tungsten trioxide (WO_3) film as the sensing element to simultaneously identify NO and NH_3 concentrations present in the fossil fuel gas exhaust. Several film parameters such as thickness, dopant (gold vs. ruthenium), doping method (post-sputter vs. co-sputter), doping amount, deposition temperature, annealment procedure and operating temperature were varied to determine their effect on the film's sensing properties. As a result, a 500Å WO_3:16Å Au film post-sputtered at 200ºC demonstrated high sensitivity and selectivity to NH_3 whereas a 1000Å WO_3 undoped film sputtered at 200ºC exhibited greater sensitivity to NO.

INTRODUCTION

The detection and measurement of flue gases are critical not only for achieving real time process control of new clean combustion systems, but also to minimize their emissions of dangerous air pollutants. Among the most dangerous of these air pollutants are nitric oxide (NO) and nitrogen dioxide (NO_2), collectively referred to as NO_x. Currently about one half of all NO_x emissions into the environment are due to power plants and industrial boilers. NO_x gas which is the precursor to nitric and nitrous acid, causes acid rain and photochemical smog and is a critical factor in the formation of ozone in the troposphere. Ground level ozone is a severe irritant, responsible for the choking, coughing and burning eyes associated with smog. Ozone often damages lungs, aggravates respiratory disorders, increases susceptibility to respiratory infections and is particularly harmful to children. Elevated ozone levels can also inhibit plant growth and cause widespread damage to trees and crops. Therefore, exceeding critical NO_x levels poses immediate health and environmental problems.

In fossil fuel combustion NO_x is formed by high temperature chemical processes from both nitrogen present in the fuel and oxidation of nitrogen in air. Typically, the NO_x emissions consist of 90-95% NO with the remainder being N_2O and NO_2.[1]

Several methods have been examined as potential control systems for the reduction of NO emissions in combustion processes including combustion control and flue gas treatment techniques such as selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR)[2,3]. SCR technology achieves the highest overall control efficiency of 60-80% NO reduction. In this process, NH_3 is uniformly injected into the flue gas stream that passes through a catalyst bed to enhance the kinetics of the NO/NH_3 reaction. This can be further improved with air staging to provide a longer residence time allowing more NO to react with the NH_3 , thus increasing NO reduction and decreasing NH_3

emissions (commonly called NH_3 slip). Although there are several chemical reactions that may take place in the catalyst bed, the most common reactions are as follows,

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O, \qquad (1)$$

$$4\ NH_3 + 6\ NO \rightarrow 5\ N_2 + 6\ H_2O, \qquad (2)$$

$$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O \qquad (3)$$

and

$$4\ NH_3 + 5O_2 \rightarrow NO + 6\ H_2O. \qquad (4)$$

Reaction (1) is the predominant reaction[1] and reduces NO into harmless nitrogen and water vapor. The reaction given in equation (3) neutralizes some of the excess NH_3 that did not fully react with the NO in equations (1) and (2) and hence decreases the NH_3 slip. An unwanted side reaction given by equation (4) oxidizes NH_3 to form water vapor and NO. This harmful oxidation process however usually takes place at elevated temperatures, and can be minimized by temperature control. If a judicious choice of NH_3 injection levels is made, NO emissions in SCR systems, as well as NH_3 slip into the atmosphere can be reduced significantly.

In order to control the precise levels of NH_3 injection, a critical need exists for an NO/NH_3 sensor system in the flue gas exhaust prior to the stack emission. The output from the sensor would be fed back to the SCR system via a real time control system to adjust NH_3 injection levels thereby maximizing NO reduction with minimal NH_3 slip into the atmosphere. Current NO and NH_3 measurement techniques, such as chromatography, chemiluminescence and infrared adsorption are very expensive and too bulky for *in situ* operation. Chemiresistive semiconducting metal oxide (SMO) films offer the technology to develop a small, inexpensive and reliable *in situ* sensor array for the simultaneous identification of NO and NH_3 present in a flue gas exhaust.

The first report on chemiresistive SMO films for gas sensing appeared in 1962[4] Since that time, considerable efforts have been made[5] to study SMO films for the detection of a variety of gases. Investigators have examined SMO films such as SnO_2 [6-15], TiO_2 [15,16], indium tin oxide (ITO) [17], ZnO [15,17,18] and WO_3 [19-22] for detecting NO, as well as ZnO [23-28], MoO_3/TiO_2 [29] and WO_3 [30-34] for detecting NH_3. WO_3 films can operate at elevated temperatures for long periods of time and selectively detect NO and NH_3 in the presence of interferent gases such as H_2, CO, CO_2, CH_4 and various other hydrocarbons. These films are also electrically and structurally stable at elevated temperatures.

The electrical conductivity of thin WO_3 films doped with metals such as gold (Au) and ruthenium (Ru), change upon exposure to NO and NH_3. The sensitivity of WO_3 to NO and NH_3 depends significantly upon film parameters such as thickness, dopant type, doping method, deposition temperature, annealing procedure and operating temperature. Furthermore, the functional relationship between sensitivity and each of these parameters is different for both gases.

THEORY

The WO_3 film conductivity changes as a function of NO and NH_3 gas concentrations. These films exhibit very fast response and recovery times and, after initial film conditioning, show no appreciable aging effects after repeated gas exposures. The basic chemical sensing mechanism involves the dissociative chemisorption of the target molecules and the formation of transitory concentrations of chemisorbed atoms on the WO_3 film surface. The rate of dissociation of the target molecules on the surface can be greatly enhanced by the addition of catalytic metals such as gold or ruthenium. Although the overall chemistry of the possible interactions of NO and NH_3 with WO_3 is complex and not well defined, certain primary interactions dominate.

In the case of NH_3 , which acts as a reducing agent (an oxygen scavenger), the carrier concentration in the film rises as a result of a decrease in adsorbed surface oxygen, as follows,

$$2\ NH_3 + 3O^-(ad) \rightarrow N_2 + 3\ H_2O + 3\ e^- \qquad (5)$$

This rise in carrier concentration within the film is then manifested as a decrease in resistivity.

Unlike NH_3, NO acts as an oxidizing agent (oxygen donor) at the temperatures of interest. Thus, reactions with NO result in an increase in chemisorbed oxygen in the film, decreasing the free carrier concentration, as follows,

$$2\ NO + 2\ e^- \rightarrow N_2 + 2\ O^-(ad). \qquad (6)$$

This decrease in carrier concentration causes the film resistivity to rise. This behavior is completely opposite to that observed with NH_3.

EXPERIMENTAL SETUP

The WO_3 sensing films were deposited on alumina and sapphire substrates by reactively sputtering a pure tungsten target in an 80/20 argon-oxygen atmosphere using an RF magnetron sputtering system. Alumina and sapphire substrates were used because they are good electrical insulators and thermodynamically stable. A DC magnetron gun was used to precisely dope the WO_3 film with gold or ruthenium to selectively catalyze the reaction with NO or NH_3. After the films were sputtered, they were subjected to an annealing process which transformed the as-deposited amorphous film into a polycrystalline film. This results in a more stable film that is chemically and conductiometrically inert to moisture and many potential interferent gases. Microheaters which controlled the temperature of the sensing film were fabricated by depositing a thin chrome serpentine structure on alumina.

The chemiresistive sensing element is placed on the surface of the serpentine microheater with silicone heat sink grease. The heater and a thermocouple are used to control the film's operating temperature. The entire apparatus is suspended on two wires attached to the sensor package to provide thermal isolation from other nearby sensors and electronics. Electrical connections to both the sensing film and microheater are made with 100µm aluminum bond wire to the sensor package. The chemiresistive sensing element and microbeater is shown in Figure 1.

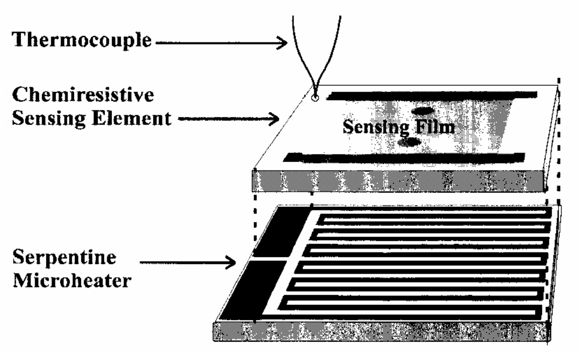


Figure 1. Chemiresistive sensing element and microheater.

In order to determine the electrical conductivity of a large number of WO_3 films exposed to a wide range of gas concentrations, a system capable of simultaneously testing and controlling up to eight sensors was designed and built. This system improved testing efficiency and insured that all films were subjected to the same gas environment during each test. A block diagram of this system is shown in Figure 2.

The sensing elements shown in Figure 1 reside inside the sealed teflon gas chamber. Two-point conductivity measurements of each sensing film are performed with an electrometer and read into the computer via a HPIB interface. The computer outputs an analog voltage to the microheater that is determined by feeding the measured film temperature through a proportional integral differential (PID) temperature control algorithm. The support electronics include power stages to supply the necessary current to all the microheaters and amplifiers that linearize the thermocouples' temperature measurements into a 10mV/°C analog signal for the computer's temperature control algorithm.

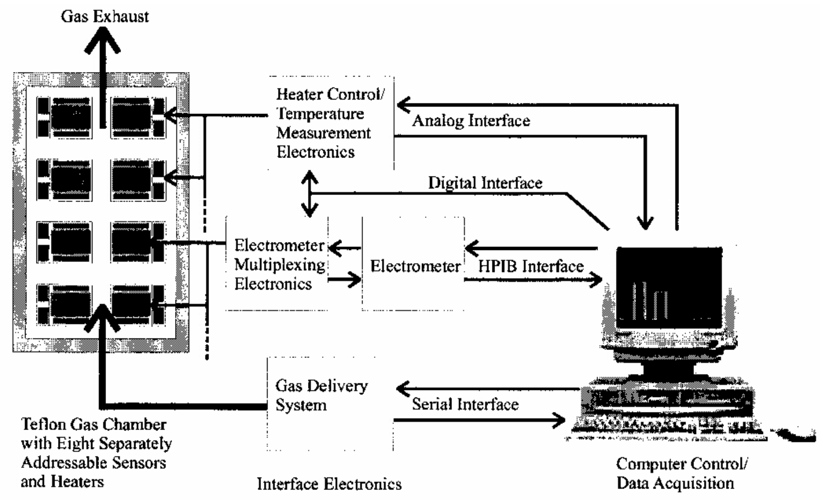


Figure 2. Block diagram of the experimental testing system.

The delivery of the NO and NH_3 gases to the sensor is achieved with the system shown in Figure 3. The apparatus consists of a bottle of the dilution gas (simulated flue gas, in this case), bottles of each test gas (NO and NH_3), an electronic three-way solenoid valve (Y-valve) and a system of mass flow controllers and plumbing. The entire system is computer controlled and is capable of delivering precise concentrations of NO and NH_3 in an atmosphere of controlled humidity for precise lengths of time. It is fully programmable and capable of running multiple tests and collecting data without user input or intervention.

RESULTS

In order to engineer the film to respond to NH_3 and NO in a fashion unique to each gas, a large number of experiments were performed to determine the film parameters that would result in responses to NH_3 and NO that were clearly different. In particular, relationships between film thickness, gold doping, annealing environment, operating temperature and electrical conductivity when the film is exposed to NH_3 and NO gas were determined. A few of these experiments are discussed below in order to demonstrate the feasibility of using WO_3 films in a sensor array to selectively detect NH_3 and NO.

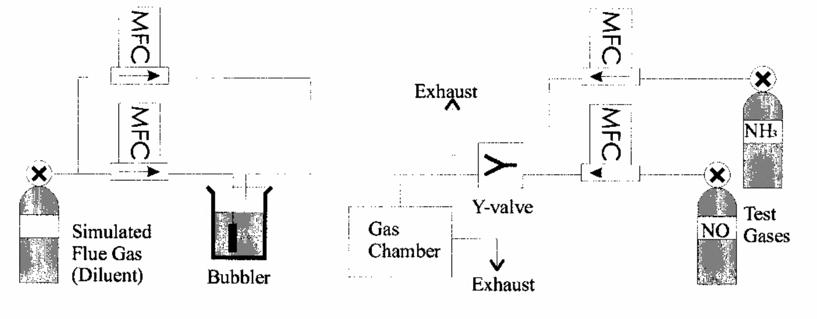
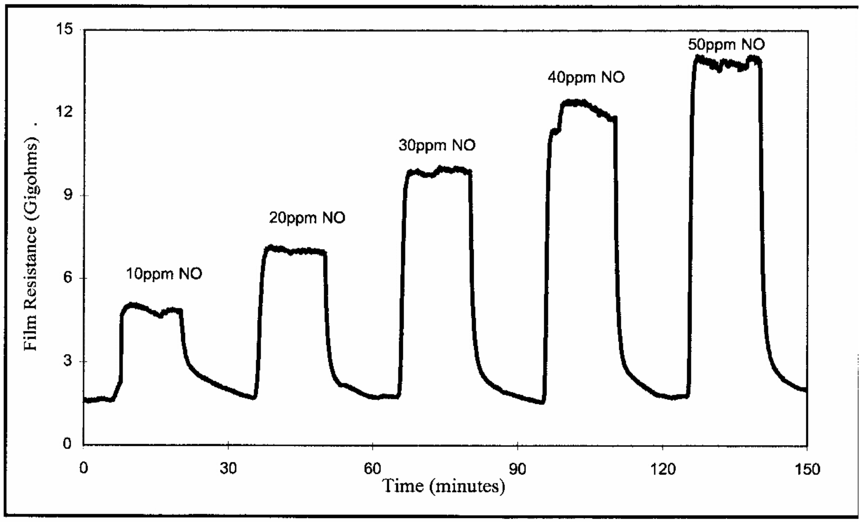


Figure 3. Gas Delivery System



A 1000Å WO_3 undoped film was sputtered at 500°C on a sapphire substrate and annealed in dry air at 300°C for 10 hours and exposed to concentrations of NO ranging from 0-50ppm at a temperature of 300°C in an environment of dry CO_2. As can be seen in Figure 4, the film demonstrated a very fast linear response to 0-50ppm NO. It also recovered to the baseline resistance when the gas was taken away which allows the sensor to measure absolute NO concentrations in real time.

Figure 4. Response of a 1000Å WO_3 film to 0-50 ppm NO at 300°C in dry CO_2

Likewise, Figure 5 shows the same 1000Å WO_3 film responding to a 50ppm pulse of NH_3 in 50% humid air. It is important to note that the response to NO is manifested as an increase in resistivity, while NH_3 results in an increase in conductivity (i.e. a *decrease* in resistivity), as predicted by equations (5) and (6) above. The film's change in resistivity is 6 times greater to 50ppm NO than to 50ppm NH_3. In fact, the film's response to only 10ppm NO was still greater than the response to 50ppm NH_3. The typical NH_3 and NO concentration ranges found in the fossil fuel combustion exhaust are 0-5ppm and 5-75ppm, respectively. Therefore, this film could selectively measure up to 10-50ppm NO in the presence of up to 50ppm NH_3.

A 500Å WO_3:16Å Au film post-sputtered at 200°C on alumina and annealed in dry air at 350°C for 5 hours was exposed to 3 pulses of 10ppm NH_3 and 3 pulses of 50ppm NO in dry air at 350 °C. Figure 6 shows the film's high sensitivity and reproducibility to 10ppm NH_3 and relatively low sensitivity to 50ppm NO. Again, the response to NH_3 is manifested as an decrease in resistivity, while NO results in an increase in resistivity. The film demonstrates adequate resolution to potentially measure NH_3 concentrations between 0-10ppm in the presence of up to 5-75ppm of NO.

SUMMARY

As a result of the tests described above, it can be deduced that the film parameters, such as thickness, doping, annealing procedure, and operating temperature significantly effect the film's sensitivity and selectivity to NH_3 and NO gas concentrations. Both, the 1000Å WO_3 undoped film operated at 300°C and the 500Å WO_3:16A An post-sputtered film operated at 350°C show potential as a two sensor array capable of simultaneously identifying concentrations of NO and NH_3. Eventually, a neural network could be trained and integrated with the chemiresistive sensor array to improve real time process control and correlate the sensors' responses to the NO and NH_3 concentrations present in a flue gas exhaust. In future work, this technology could be extended to include other combustion gases such as SO_x and H_2S

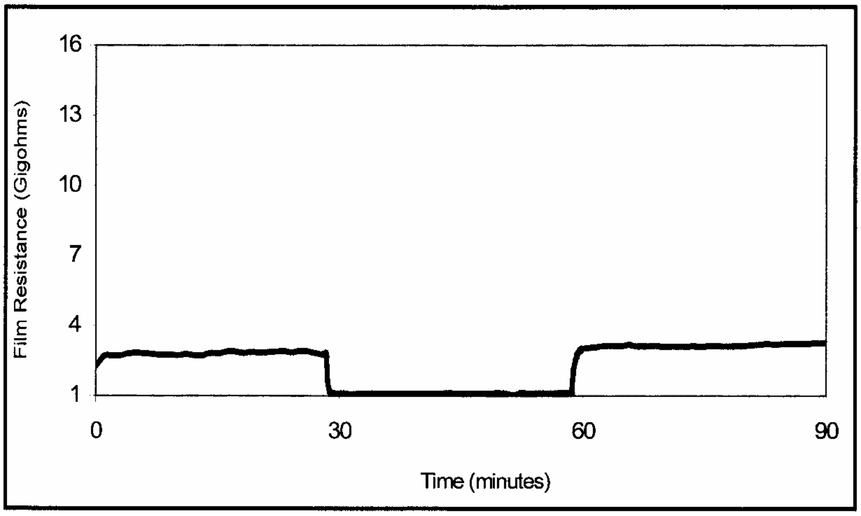
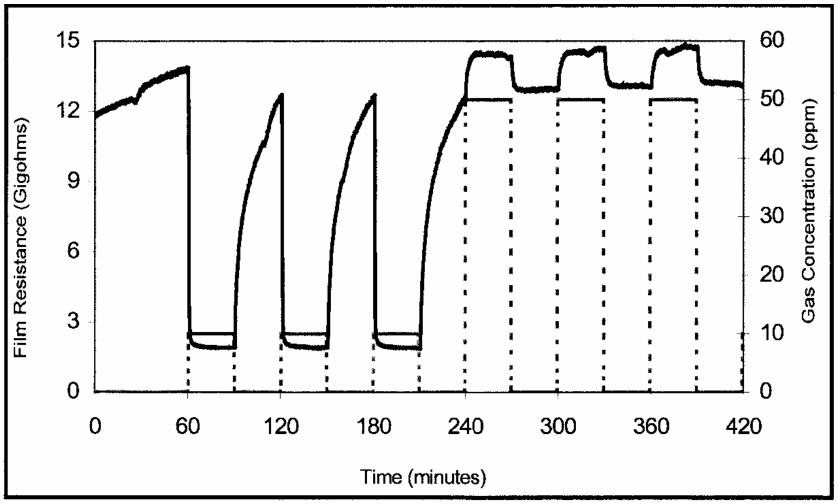


Figure 5. Response of 1000Å WO_3 film to 50ppm NH_3 at 300°C in humid air.



ACKNOWLEDGMENTS

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Figure 6. Response of a 500Å WO_3:16Å Au film to (3) 10ppm pulses of NH_3 and (3) 50ppm pulses of NO at 350°C in humid air, respectively.

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RELEVANCE OF ENANTIOMERIC SEPARATIONS IN ENVIRONMENTAL SCIENCE

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A significant number of all organic chemicals that are released into the environment are racemic mixtures. Most environmental regulations and scientific environmental studies treat racemic mixtures as though they were single, pure compounds. This can lead to incorrect toxicological, distribution, degradation and other data. A series of new enantioselective analytical techniques have been developed that allow the facile separation and quantitation of chiral compounds of environmental importance.[1] Table 1 shows a typical example of the disparate biological activities of paclobutrazol stereoisomers.[2]

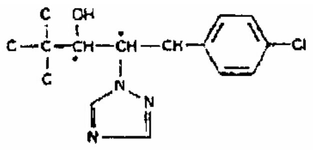

Table 1. Biological activity of paclobutrazol diastereoisomers and enantiomers.

Compound	Fungicidal activity (cereal mildews and rust)	Plant growth regulatory activity (apple seedlings)
2RS,3RS	High	High
2R,3R (+)	High	Low
2S,3S(-)	Low	High

Note: The 2R,3R(+) enantiomer has a high fungicidal but a low plant growth regulatory activity. For the 2S,3S (-) enantiomer the reverse situation holds true. Separation of the enantiomers implies separation of the desired and the undesired action

We have examined the enantioselective biodegradation of chlorinated pesticides and the herbicides dichlorprop and mecoprop. While it is known that the herbicidally active enantiomer is the (+) enantiomer for both herbicides, and fate of each enantiomer in broadleaf weeds and grass has not previously been reported. Both dichlorprop and mecoprop are sold as racemic mixtures and are among the most commonly used herbicides for the control of broadleaf weeds in grass. This presentation compares the biodegradation of each enantiomer of dichlorprop and mecoprop in several types of broadleaf weeds and common grasses. The results indicate that one enantiomer is degraded faster in weeds, while both enantiomers degrade at equal rates in grass.

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DEVELOPMENT OF AEROSOL MASS SPECTROMETER FOR REAL TIME ANALYSIS OF PAH BOUND TO SUBMICRON PARTICLES

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Polycyclic aromatic hydrocarbon (PAH) are mutagenic pollutants formed as by-products of combustion. Measurements of the distribution of PAH species with different aerosol particles of different sizes are critical for a complete understanding of the environmental fate of the human exposure to PAH. We present here an aerosol mass spectrometer (AMS) designed to simultaneously measure particle size, particle number density and size-resolved particle composition for volatile and semi-volatile compounds. The instrument combines a unique aerodynamic sampling inlet which focuses the particles into a narrow beam and efficiently transports them from atmospheric pressure into a vacuum chamber where particle mass/size is determined by time-of-flight (TOF) measurement. Size-resolved single particles are flash vaporized on a heated filament and ionized by resonance enhanced multi-photon ionization (REMPI) using an excimer laser (248 nm). The PAH ions are detected by a molecular TOF mass spectrometer. The ionization process is highly selective for aromatic PAH.

The AMS described here provides size-resolved single particle composition detection down to 50 nm. Molecular mass spectra for a number of PAH aerosols have been measured. The sampling efficiency and the size resolution of the instrument have been investigated using a differential mobility analyzer (DMA) and condensation nucleus counter. Size resolution defined as Dp/Dp = 4 (where Dp = particle diameter) has been measured for tenth micron size particles with sampling efficiencies approaching unity, and found to be about 25%.

REAL-TIME TRACE DETECTION OF ELEMENTAL MERCURY AND ITS COMPOUNDS

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Introduction

Emission of elemental mercury [Hg] vapor and volatile mercury compounds [e.g. $HgCl_2$, $Hg(CH_3)_2$] from combustion and other processes is an important environmental issue [Von Burg and Greenwood, 1991]. The present research addresses the need to develop real time stack monitoring of emissions of Hg and its compounds. Such continuous emission monitor (CEM) technology would enable identification of peak emission events and the possibility of corrective action. Realistic emission inventory will enable regulatory agencies to better assess health risks associated with future siting of emission sources, such as waste incinerators.

To be useful to a wide range of applications, the CEM should be capable of detection in the range of 1-5000 $\mu g/m^3$, with an ultimate sensitivity limit on the order of 0.1 $\mu g/m^3$ (ca. 10 pptv). Current best technology for Hg detection uses cold vapor trap resonant atomic fluorescence [Tekran, 1998]. However, this technology provides no information on mercury compounds.

In this work, detection of mercury compounds is based on photo-fragment fluorescence (PFF) excited by deep ultraviolet (UV) light. The fluorescence spectra can facilitate identification of the original mercury compounds. Photo-fragment fluorescence has been successfully applied for the gas-phase analysis of $HgCl_2$, $Hg(CH_3)Cl$, and HgI_2 (Barat and Poulos, 1998).

The detection for Hg uses Doppler-shifted resonant atomic fluorescence excited by a UV laser or a low pressure mercury lamp. The Doppler-shifted fluorescence will be separated from the unshifted background signal by use of an optically dense Hg vapor filter precisely matched to the spectral linewidth of the source. An alternative to the vapor filter is precise use of time gating to distinguish the nearly instantaneous background scattering from the relatively long fluorescence signal.

The experimental program involves three stages. In the first, a static cell (no flow) containing mercury (elemental or compound) vapor is probed with a deep UV laser to generate spectra. An atmospheric pressure flow cell is used in the second stage. The third stage utilizes the expanding jet.

Compounded Mercury

In general, mercury compounds absorb light strongly below 250 nm [Gowenlock and Trotman, 1955], and these absorption bands are generally dissociative. In PFF, a photolyzing UV photon dissociates the target molecule into fragments, some of which are imparted with excess energy. The energy might then be lost by fluorescence:

$$A\text{-}B \xrightarrow{h} A + B^* \qquad (1a)$$

$$B^* \longrightarrow B + h' \qquad (1b)$$

where A and B can be atoms or polyatomic species. The fragment identities and distributions, as revealed in the fluorescence spectrum, can, in principle, provide information on the parent species, in a manner analogous to mass spectrometry and other fragmentation spectroscopies.

For example, Figure 2 shows the PFF spectrum from 193 nm excimer laser excitation of $Hg(CH_3)Cl$ vapor in a static cell (Figure 1). Two features are evident: atomic Hg emission lines at 546 and 579 nm; and a broad continuum assigned to the B-->X system of HgCl** excited state (Mandl and Parks, 1978; Whitehurst and King, 1987). Likely photochemical processes resulting in these observations are:

$$Hg(CH_3)Cl \xrightarrow{h} HgCl^{**} + CH_3 \qquad (2)$$
$$HgCl^{**} \longrightarrow HgCl + h\ ' \qquad (2a)$$
$$\longrightarrow Hg + Cl \qquad (2b)$$

Steps (2a) and (2b) are clearly implicated, but the origin of the Hg atomic emission lines is open to question. Focussing the laser beam increases the emission from Hg, and generates the blue emission at 431 nm from CH*.

The lowest concentration of mercury compound [$Hg(CH_3)Cl$] measured in the static cell was approximately 50 µg/m^3. Using reasonable improvements in optics and electronics, it is estimated that the limit-of-detection can be lowered by at least a factor of 500.

The concentration of the target compound is related to the fluorescence intensity from a hot fragment. Excitation laser energy of about 2 mj/pulse at a repetition rate of 10 Hz at 222 nm was applied to $HgBr_2$ vapor (in Argon) in an atmospheric pressure flow cell (Figure 3). The PFF was monitored using a photomultiplier tube and narrow interference filters centered at 254 nm - a strong Hg* emission line - (see Figure 4). Excellent linearity was obtained over a wide concentration range. Similar results were obtained using a compact monochromator + CCD system.

The supersonic jet spectroscopy (to be discussed in the next section) is expected to further improve sensitivity of PFF detection. Spectra will be sharpened, leading to better discrimination of fragment vibrational structure. Quenching by O_2 will be reduced due to the low pressure.

Elemental Mercury

Atomic Fluorescence Spectroscopy (AFS) is a highly sensitive spectroscopic marker for elemental Hg detection. Current AFS instruments (e.g. Tekran, 1998) use a cold vapor trap for collection + concentration of the air sample, purging (to remove O_2), desorption, excitation with an Hg vapor lamp (253.7 mn), and then measurement of the resonant fluorescence (at the same wavelength). Sensitivity is limited by the elastically scattered light from the exciting source.

The technique under study, shown in Figure 5, will expand the Hg-contaminated air stream across a supersonic nozzle into a high vacuum chamber. Light at 253.4 rim will be directed across the jet. Atomic Hg fluorescence will be Doppler-shifted by between 1 and 3 GHz due to the jet motion. Total collected light, comprised of the shifted fluorescence and stray elastic scattering, will be passed out of the vacuum chamber and through (Figure 6) an optically dense, sharp cut-off Hg vapor filter (centered at the excitation wavelength) to reduce elastic scattering while transmitting the fluorescence signal (Miles, 1991; Finkelstein, et al., 1994).

The expansion reduces the collision rate of Hg* with O_2, so collisional quenching and collisional broadening are both substantially reduced. The low temperature associated with this expansion further reduces the fluorescence linewidth, enhancing the performance of the Hg vapor filter.

In the absence (or in conjunction with) the atomic filter, time gating of the collected signal offers an alternative means to extract the fluorescence signal from the scattering background. It has been observed in the atmospheric pressure flow cell experiments with $HgBr_2$ that scattering is essentially instantaneous, lasting for the duration of the laser pulse (i.e. 10 nanoseconds). The relatively long lifetime for Hg* (117 nanoseconds at 253.7 nm - Dodd et. al., 1970) results in the fluorescence signal appearing as a long-tailed shoulder on the scattering signal. Prudent placement of the signal detection gate, as well as subtraction of the background signal measured in the absence of Hg vapor, should allow for extraction of the desired fluorescence signal.

Quality Assurance / Performance Assessment

For comparison of time-averaged test concentrations, the mercurycontaining sample stream will be diverted to a reference method, such as optical absorption. Testing of the research technology will consist of obtaining data on five performance measures:

Relative Accuracy: the absolute mean difference between the metals concentration determined by the monitor and that determined by the reference method, plus a 2.5 percent uncertainty confidence coefficient based on a test series.

Calibration Drift: the difference in the monitor output reading from the established reference value after a stated period of operation. The reference value is established by a calibration standard which has a concentration nominally 80 percent or greater of the full scale reading capability of the monitor.

Zero Drift: calibration drift when the reference value is zero.

Response Time: the time interval between the start of a step change in the concentration of the monitored gas stream and the time when the output signal reaches 95 percent of the final value.

Detection Limit: three times the standard deviation of nine repeated measurements of a low-level (near blank) sample.

Acknowledgement

The author thanks Dr. Arthur T. Poulos, President of Poulos Technical Services, Inc., for his significant contributions to this research. The author would also like to thank the U.S. Environmental Protection Agency - National Center for Environmental Research and Quality Assurance for its financial support of this work (Grant # R-825380-01-0), and grant project officer Mr. William Stelz for his administrative guidance.

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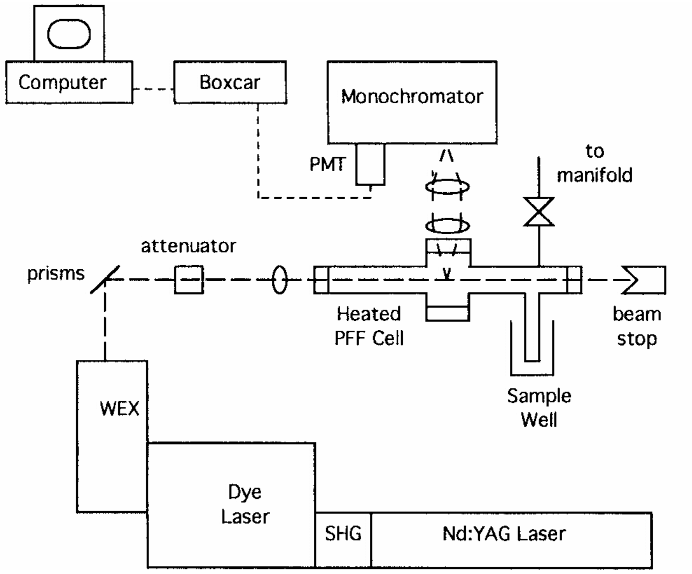

Figure 1. Research Apparatus #1: Static Cell for Atomic and Photo fragment Fluorescence

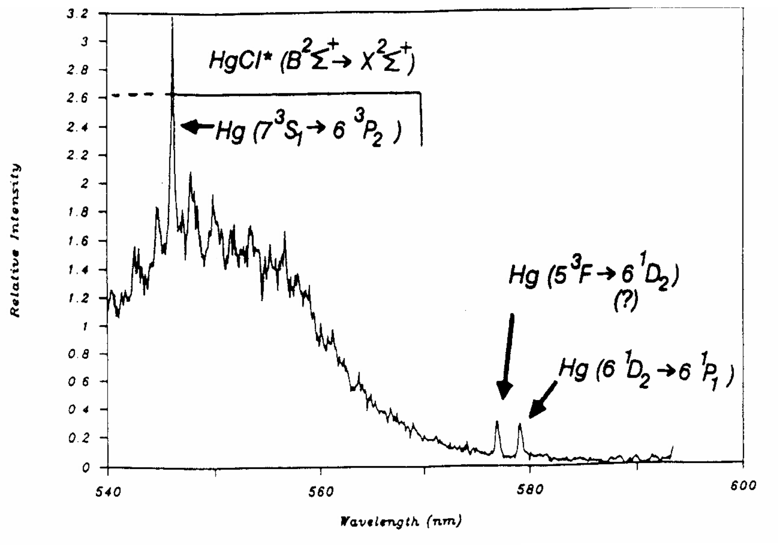

Figure 2a. PFFS of Hg(CH$_3$)Cl
193 nm excitation - not focused

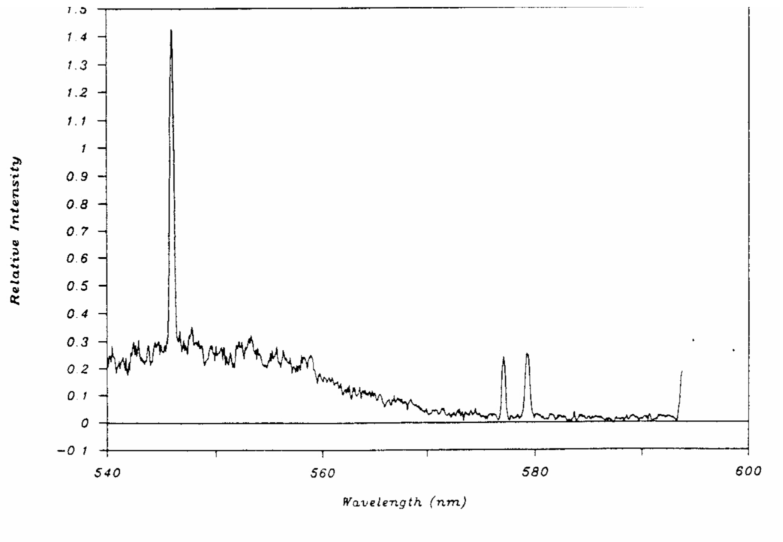

Figure 2b. PFFS of Hg(CH$_3$)Cl
193 nm excitation - focused

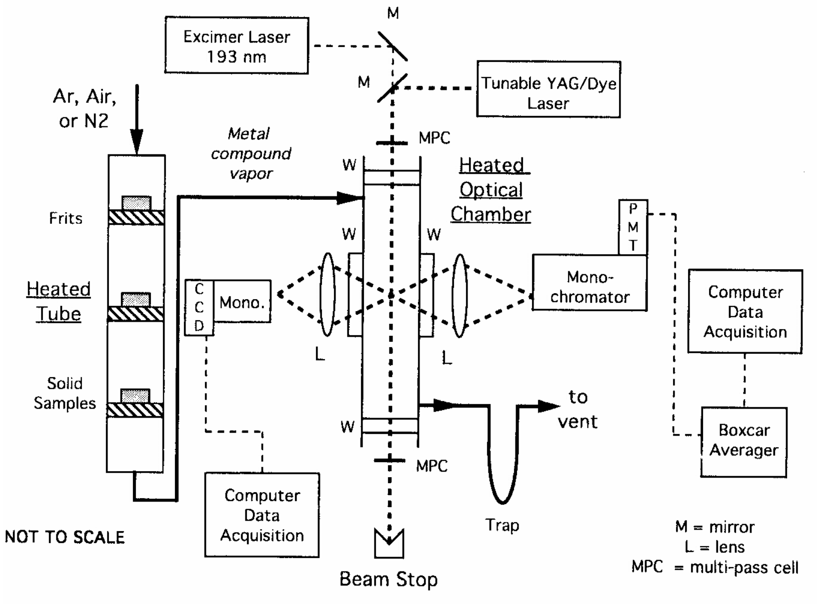

Figure 3. Research Apparatus #2: Flow Cell for PFF

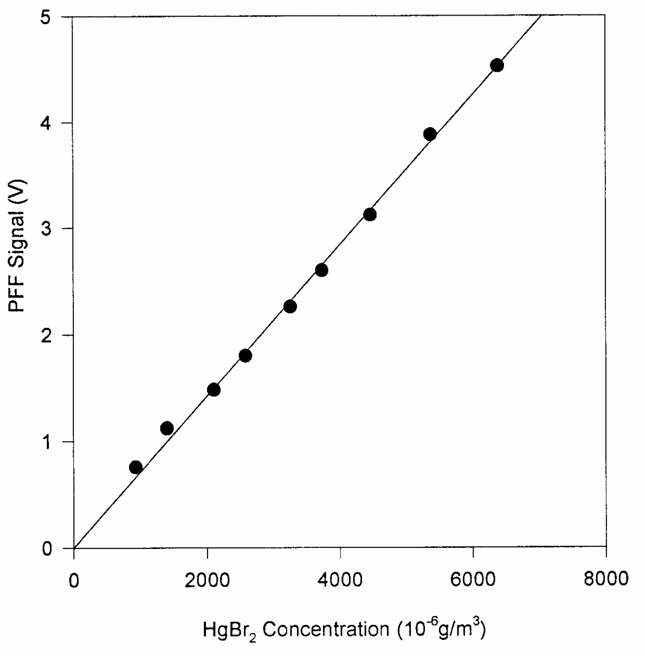

Figure 4. Photofragment Fluorescence (PFF) Signal vs. HgBr$_2$ Concentration

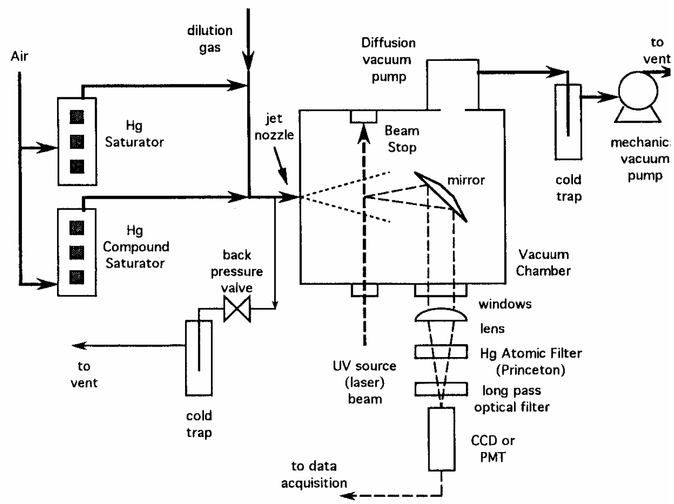

Figure 5. Apparatus #3: Atomic Fluorescence and Compound PFF in Vacuum

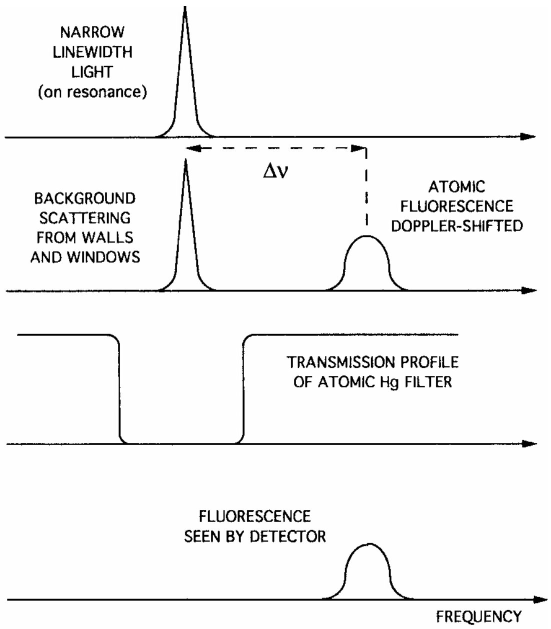

Figure 6. Doppler-shifted Resonant Fluorescence

ORTHOGONAL BACKGROUND SUPPRESSION TECHNIQUE FOR EPA'S FIELD INFRARED DATA PROCESSING

Blaterwick

NO ABSTRACT AVAILABLE

DEVELOPMENT OF A CONTINUOUS MONITORING SYSTEM FOR PM_{10} AND COMPONENTS OF $PM_{2.5}$

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ABSTRACT

While particulate matter with aerodynamic diameters below 10 and 2.5 µm (PM_{10} and $PM_{2.5}$) correlate with excess mortality and morbidity, there is evidence for still closer epidemiological associations with sulfate ion, and experimental exposure-response studies suggest that the hydrogen ion and ultrafine ($PM_{0.15}$) concentrations may be important risk factors. Also, there are measurement artifacts in current methods used to measure ambient PM_{10} and $PM_{2.5}$, including negative artifacts because of losses of sampled semivolatile components (ammonium nitrate and some organics) and positive artifacts due to particle-bound water. In order to study such issues, we are developing a semi-continuous monitoring system for PM_{10}, $PM_{2.5}$, semivolatiles (organic compounds and NH_4NO_3), particle bound water, and other $PM_{2.5}$ constituents that may be causal factors. PM_{10} is aerodynamically sorted into three size-fractions: 1) coarse (PM_{10}-$PM_{2.5}$); 2) accumulation mode ($PM_{2.5}$-$PM_{0.15}$); and 3) ultrafine ($PM_{0.15}$). The mass concentration of each fraction is measured in terms of the linear relation between accumulated mass and pressure drop on polycarbonate pore filters. The $PM_{0.15}$ mass, being highly correlated with the ultrafine number concentration, provides a good index of the total number concentration in ambient air. For the accumulation mode ($PM_{2.5}$-$PM_{0.15}$), which contains nearly all of the semivolatiles and particle-bound water by mass, aliquots of the aerosol stream flow into system components that continuously monitor sulfur (by flame photometry), ammonium and nitrate (by chemiluminescence following catalytic transformations to NO), organics (by thermal-optical analysis) and particlebound water (by electrolytic hygrometer after vacuum evaporation of sampled particles). The concentration of H^+ can be calculated (by ion balance using the monitoring data on NO_3^-, NH_4^+, and $SO_4^=$).

OBJECTIVES

Background

Particulate matter (PM) is an ambient air criteria pollutant that does not, as listed, have any specific compositional definition. When initially defined (in 1971) as total suspended particulate matter (TSP), it had no specific particle size distinction either. The TSP inlet cut-size was determined by the inlet aspiration efficiency, whose upper 50% cut-size (20-50 gm) varied with ambient wind speed and direction. The 1987 PM_{10} National Ambient Air Quality Standard (NAAQS) revision was defined in terms of the mass concentration of PM aspirated by a non-directional and wind speed insensitive inlet with a 50% sampling efficiency at ~10 µm aerodynamic diameter. The PM_{10} cut approximates that of the normal human upper respiratory tract during oral inhalation, so that the sampled particles represent those that can penetrate to the thoracic airways (tracheobronchial tree and more distal gas-exchange airways). Particles depositing along the tracheobronchial tree (lung conductive airways) can exacerbate asthma and cause bronchitis and bronchial cancer, while those depositing in the gas-exchange airways can cause lung fibrosis, emphysema and peripheral lung cancers. Particles that are retained in the lung airways can cause persistent local irritation and/or dissolve and be translocated to more distant organs via the bloodstream.[1,2]

Neither the PM_{10} nor the TSP NAAQS made any distinction as to the chemical composition of the particles sampled. In terms of composition, there is a relatively clear distinction between coarse and fine particles in the ambient air, as illustrated in Figure 1.

The coarse mode of the ambient aerosol is generally composed of soil and soil-like dust and ash particles generated and/or dispersed by mechanical forces. It is typically dominated by basic mineral oxides in particles larger than ~1.0 μm. By contrast, the fine mode particles are generally derived from gas-phase precursors, which form in the atmosphere as ultrafine (nuclei mode) particles after chemical transformations. The transient nuclei mode particles rapidly coagulate and coalesce to form larger accumulation mode particles in the light-scattering range (0.1 to 1 pm), are persistent in the air for many days, and contain almost all of the sulfate, ammonium and hydrogen ion, as well as most of the nitrate ion and carbonaceous particles. Size-selective ambient air samplers have been developed to collect the coarse mode and fine mode particles separately, typically with a relatively sharp size-cut at 2.5 μm in aerodynamic diameter ($PM_{2.5}$). When using a 2.5 μm cut, the fine mode includes essentially all of the sulfates and organics, but also includes the lower tail of the coarse mode.

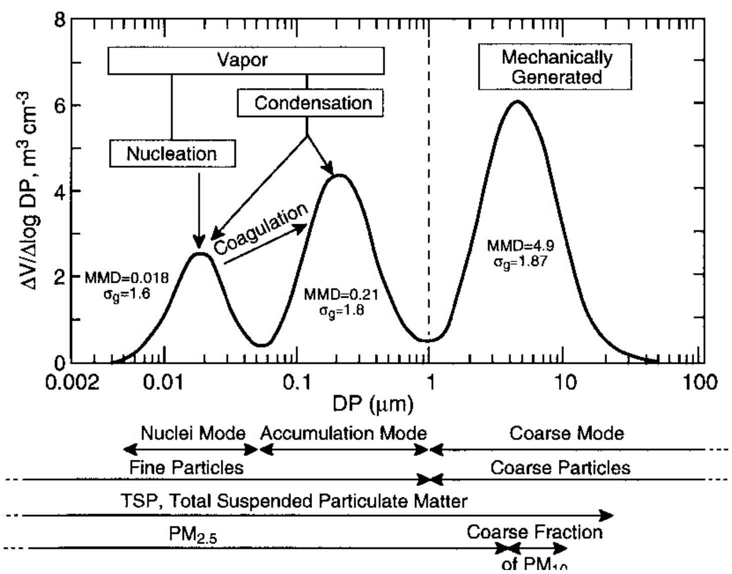


Figure 1. Measured mass size distribution showing particles in nuclei and accumulation modes of fine particles. Also shown are transformation and growth mechanisms (e.g., nucleation, condensation, and coagulation).

From some epidemiological studies, there is suggestive evidence that the excess mortality and morbidity associated with elevated PM was more closely correlated with $PM_{2.5}$ than with PM_{10}.[3] The fine particle mass in the eastern U.S. is dominated by sulfates ($SO_4^=$), and the epidemiological evidence suggests that excess mortality and morbidity are as well or better correlated with ambient $SO_4^=$ than with $PM_{2.5}$.[4] The $SO_4^=$ is, in turn, highly correlated with aerosol acidity (H^+), a more likely causal factor than SOC on the basis of controlled exposure studies in humans and animals.[4]

At this time, the actual causal factor(s) for the excess mortality and morbidity are not clearly established. However, in 1997, the EPA adopted both 24 hr and annual average $PM_{2.5}$ standards on the basis that $PM_{2.5}$ is the best currently available surrogate index for the health effects associated with ambient air PM.[5] At the same time, EPA retained the PM_{10} NAAQS, with some relaxation in stringency, because of residual concerns about the health risks from the coarser particles that deposit on lung conductive airways, and may cause or exacerbate asthma, bronchitis, or bronchial cancer.[5]

Currently available monitoring methods, which are based on filter sampling of ambient PM_{10} or PM_{25}, with subsequent determination of sampled mass, have significant limitations for the accurate determination of ambient PM mass concentrations. Some of the ambient PM is semi-volatile, especially ammonium nitrate and some of the organic constituents. Sampled PM mass can be lost, especially when the temperature is elevated during the sampling and/or prior to analysis. Nitrate (NO_3^-) can also be lost from the sampling filter after collection of acidic sulfates as the H^+ combines with NO_3^- to form nitric acid vapor (HNO_3) that is carried off by air passing through the filter. There can be positive artifacts as well, most notably due to water of hydration at high ambient humidities. Their associated water may contribute to the measured fine particle mass without adding to the health risk. In view of these considerations, there is a need to be able to determine the concentrations of several key species within the accumulation mode particles that may be either candidate causal factors or likely sources of sampling artifacts. The most important of these aerosol components are $SO_4^=$, NO_3^-, NH_4^+, H^+, semi-volatile organics (SVOC) and water vapor.

There is also some concern about the health effects of ultrafine particles (those less than 0.1 μm diameter). Some animal studies indicate that extremely small mass concentrations of ultrafines 25 μg/m^3) can cause excess mortality and pathological changes after brief exposures[6,7] Evidence for an important role for ultrafines is reported by Peters et al.,[8] who found somewhat closer associations between reduced pulmonary function in nonsmoking adult asthmatics with number concentration than with $PM_{2.5}$ mass concentration. Finally, it remains possible that the effects of $PM_{2.5}$ may really be due to its total mass concentration and not to any of its specific chemical constituents. Thus, it is important to accurately determine the overall mass concentration.

Design Objectives

These considerations lead to our design objectives for the continuous monitoring of PM_{10} and $PM_{2.5}$. The concentrations of components to be measured separately are: 1) coarse mode particle mass (i.e., PM_{10}-$PM_{2.5}$); 2) fine mode sulfate ($SO_4^=$); 3) fine mode nitrate (NO_3^-); 4) fine mode ammonium (NH_4^+); 5) fine mode organic carbon (OC) and elemental carbon (EC); 6) fine mode water (H_2O); 7) fine particle mass ($PM_{2.5}$); and 8) ultrafine mode mass ($PM_{0.15}$).

The sum of mass components 1 and 7 equals PM_{10} mass. H^+, a PM parameter of interest can also be derived from the monitoring data. As shown in Figure 2, the milliequivalent sum of the accumulation mode anions ($SO_4^=$ and NO_3^-) is equal to the sum of the cations (NH_4^+ + H^+). Thus, we can estimate H^+ concentration by net ion difference. For ultrafines, the parameter of interest may be number concentration rather than mass concentration. However, as indicated in Figure 3, the mass and number concentrations for particles below 0.1 μm are highly correlated. Thus, the ultrafine number concentration can be reliably estimated from the corresponding measured mass concentration. Alternatively, the number concentration can be directly measured using a condensation nucleus counter (CNC).

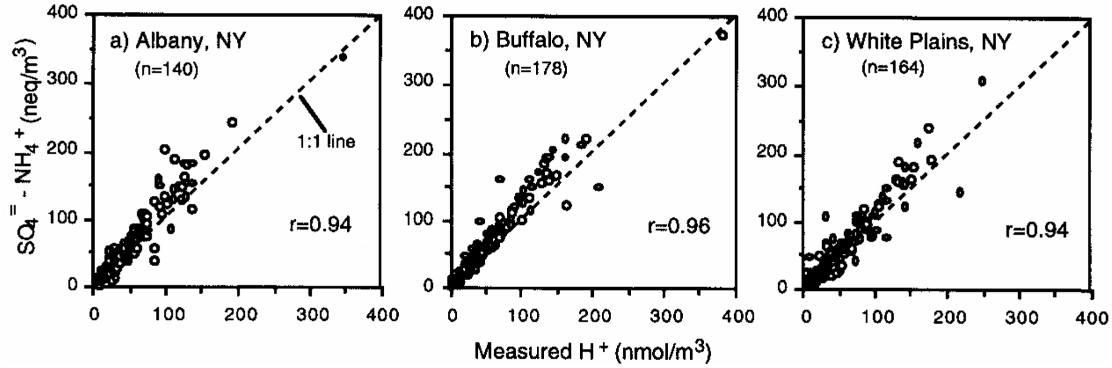


Figure 2. Comparison of estimated H^+ (via ion difference) to directly measured H^+ (via pH) for data collected on Teflon filters at 3 NYDEC sites (June-August, 1988 and 1989). Unpublished data from Dr. G.D. Thurston, NYU.

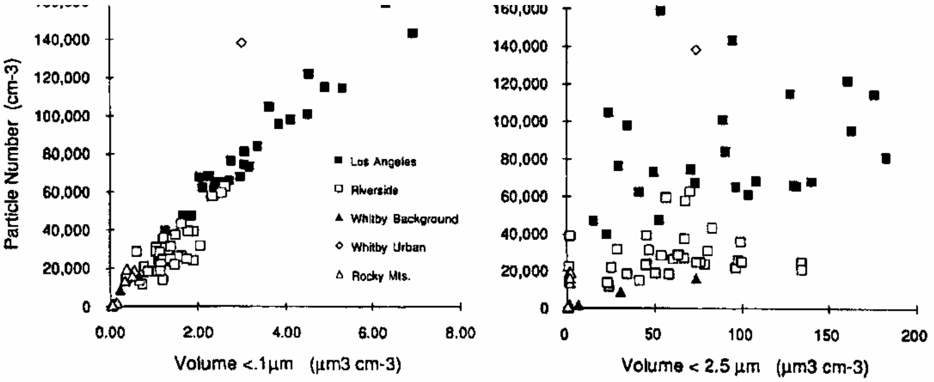


Figure 3. Relationships between particle number and volume concentrations: Left panel for ultrafine particles (smaller than 0.1 μm); right panel for fine particles (smaller than 2.5 M). From: USEPA (1996).

Design Concept

The overall design concept is illustrated schematically in Figure 4.

The PM_{10} inlet limits access to those particles that can penetrate into the human thorax. This is followed by a virtual impactor with a 2.5 μm cut-size. The coarse particle mode is directed onto a spot on a polycarbonate pore ucleporeTM) filter tape using the filter resistance method developed by Koutrakis et al.[9] After a suitable sampling interval and determination of particle mass collected, the tape spot is mechanically advanced for sample storage and presentation of a fresh filter surface for the next sampling interval. The fine particle fraction (suspended in 29 lpm of the inlet flow) is carried into a second virtual impactor with a 0.15 µm cut-size (lowest practical cut-size). The smaller (ultrafine) particles are collected on a filter spot on a sequential filter sampler for periodic mass concentration analyses in a manner similar to that used to measure the coarse particle fraction. The extension of the method of Koutrakis et al.[9] to ultrafine particles is described in detail later in this paper. The accumulation mode particles (0.15 to 2.5 µm), suspended in 2.9 lpm of the inlet air, are directed into: 1) a stream of 1.8 lpm leading to the aerosol water detector; and 2) a stream of 1.1 lpm leading to the inlets of the continuous detectors for accumulation mode aerosol components of primary interest, i.e., $SO_4^=$, NO_3^-, NH_4^+, OC, and EC. A third filter tape sampler draws off 0.2 lpin of the fine particle ($PM_{2.5}$) stream into a filter tape sampler for the determination of the overall mass concentration of $PM_{2.5}$.

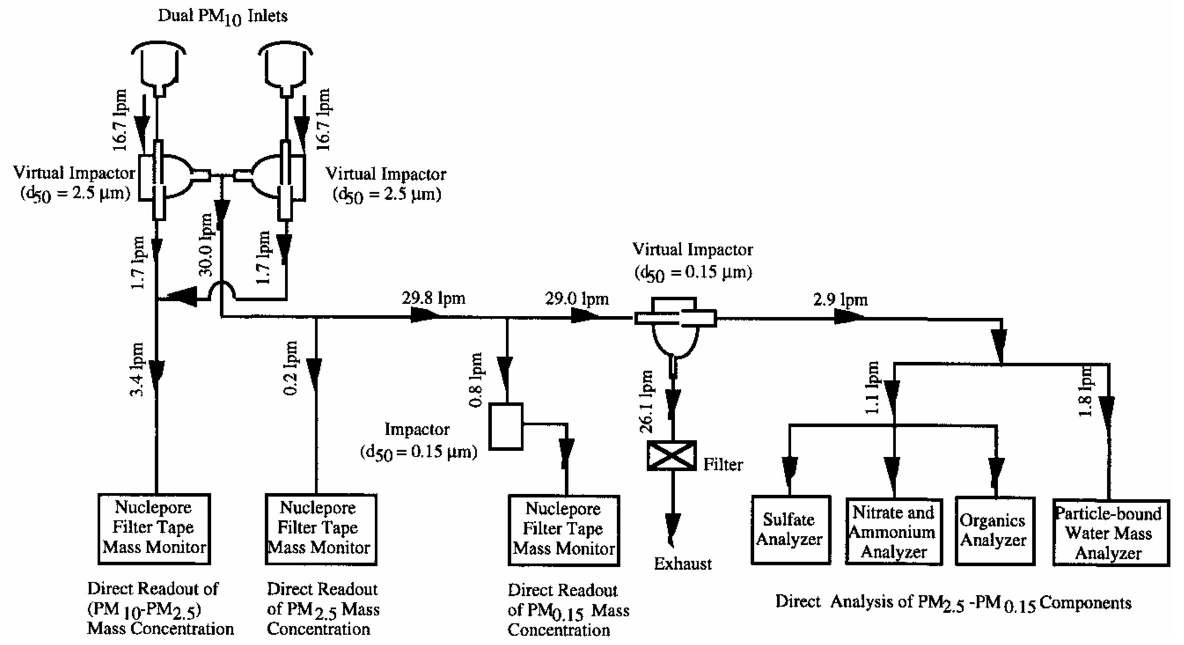


Figure 4. Overview of the system for continuous measurement of PM 10 and components of $PM_{2.5}$.

With the exception of the aerosol water and particulate mass detectors, each of the continuous monitors uses well established detection methods available in widely used commercial instruments. Similarly, the PM_{10} inlet and 2.5 µm virtual impactor are widely used and commercially available. A 0.15 µm virtual impactor was designed and tested by Sioutos et al.[10]

Monitoring System Elements Based on Commercial Available Equipment

1) Flame-Photometric Detector (FPD) for Aerosol Sulfate: The Meloy Model 285 FPD can be used to measure total concentration of sulfur in the aerosol by using PbO diffusion denuders at the inlet to remove ambient vapors, such as SO_2, H_2S, and mercaptans. The sulfur in the aerosol is, with rare exceptions, due to its presence in sulfates (H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$). Thus, the sulfate ion mass concentration is essentially equivalent to three times the measured sulfur concentration. This application of the FPD has been described by Cobourn et al.[11] and Allen et al.[12] The instrument detection limit is 1 ppb (4 µg/m^3 $SO_4^=$) with a sampling flowrate of 180 ml/min. Since the sample is preconcentrated 10 times by means of a 0.15 gm virtual impactor before analysis, the detection limit is ~0.4 µg/m^3 for accumulation mode particulate SO_4 in ambient air.

2) Thermal-Optical Technique for Measurement of Aerosol Organic Carbon (OC) and Elemental Carbon (EC): For measurement of aerosol organic and elemental carbon, we plan to adopt an *in situ* aerosol carbon analysis method developed by Turpin et al.[13] The method combines the sampling function of a two-port parallel filter sampling technique with the analytical function of a thermal-optical carbon analyzer,[14,15] and was employed in the Carbonaceous Species Method Comparison Study (CSMCS) in Glendora, California, in the summer of 1986, for side by side measurement of sub-2.5 gm aerosol carbon concentrations with other conventional sampling and analysis methods.[16] The detection limit of the method was reported to be as low as 0.2 µg carbon with a precision of about 3%.

3) <u>PM_{10} Inlet and $PM_{2.5}$ Virtual Impactor</u>: We use 16.7 liter/min (lpm) inlets and 2.5 μm virtual impactors from Series 241 Graseby-Andersen PM_{10} Manual Dichotomous Samplers. They separate the 16.7 lpm of inlet flow into: 1) a 1.7 lpm stream containing the PM_{10} coarse-mode fraction along with 10% of the fine fraction; and 2) a 15 lpm stream containing 90% of the fine PM fraction.

Monitoring System Elements Under Development and/or Undergoing Evaluation Detail in this Research

1) <u>Particulate Mass Concentration Monitors:</u> We are using the newly developed method of Koutrakis et al.,[9] in which the mass accumulated on a polycarbonate pore (Nuclepore™) filter can be shown to be directly proportional to the pressure drop across that filter. The basis for the method is that the particles are collected at the entries to and within the pores of the Nuclepore™ filter by interception or Brownian diffusion, rather than on the surfaces between the pores by impaction. The flow through the pores is restricted by the presence of the collected particles in proportion to their volume.

For the coarse particles (PM_{10}-$PM_{2.5}$), a Nuclepore™ filter with 10 μm pores is being used, while for the fine mass 2 μm pores are used. In order to measure the mass concentration of ultrafine particles, we use a modified system that uses a filter with 0.2 μm pores. The 0.2 μm pore filter has a relatively high baseline flow resistance, and very small mass increments due to collected ultrafines will markedly increase the resistance, providing a very sensitive measure of the mass concentration of ultrafine particles.

Design and Validation of the Ultrafine Mass Monitors

The ultrafine, mass monitor (CPMM-U) consists of two parallel channels, four capillary pore filters (N1 ... N4), and two HEPA filters (Figure 5). In addition, needle valves and flow meters are used to control and monitor the flow rates in each channel. Two sensitive pressure transducers (T1 and T2) are used to measure the change in pressure drop at two locations along each channel as shown in Figure 5. The measured pressure drops can be related to the mass loading of the first capillary pore filter of the measurement channel. The left channel, which has a capillary pore filter exposed to ambient particles, is the measurement channel. The right channel, with both capilliary pore filters behind the HEPA filter, is the reference channel.

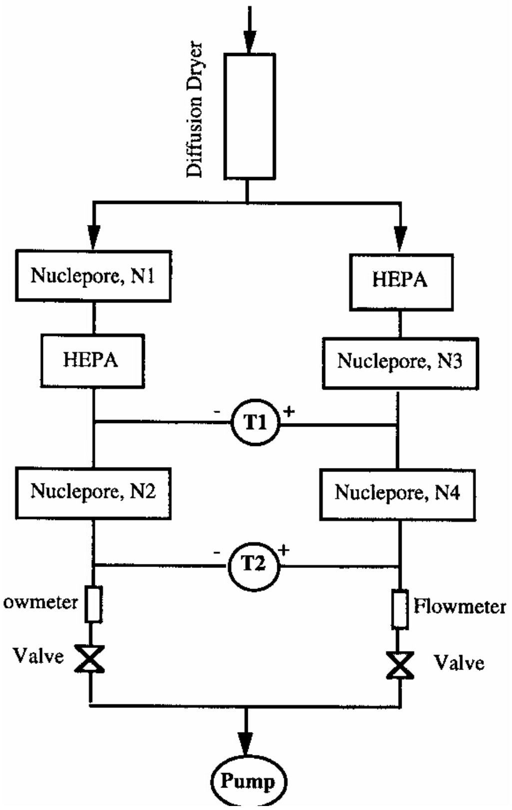


Figure 5. Schematic layout of the basic elements of the system for the measurement of the mass concentration of the ultrafine function of ambient air particulate matter. The increased flow resistance across the N1 Nuclepore filter is proportional to the accumulated mass and number of ultrafine particles.

The pressure drop across a capillary pore filter is affected by relative humidity, temperature, flow rate, and the static pressure at the entrance of the filter. The effect of any one of these factors can exceed the change in pressure drop due to particle loading. While N2 serves as a reference to eliminate the fluctuations in relative humidity, temperature and flowrate, a one-channel design has serious limitations. First, since the range of the change in pressure drop across N1 is very small (<5%) in comparison to the overall pressure drop of the filter, it is difficult to accurately measure the change in pressure drop due to particle loading. Also, it cannot be assumed that N2 operates at the same conditions as N1. This requirement is approximately satisfied for humidity, temperature, and flow rate. However, the pressure at the entrance of N2 may be different if N1 causes a significant pressure drop, as in the case of using a capillary pore filter with a small pore size. A two-channel design greatly improves on these limitations.

To measure the mass of ultrafine particles, a very small pore size is needed in order to match the size of particles of interest and optimize the sensitivity of the instrument. This results in a very high baseline pressure drop. The typical pressure drop in the Koutrakis[9] CPMM design using a 2 μm pore size was ~12 inches of water, while the pressure drop in CPMM-U using a 0.2 μm pore size is ~70 inches. Two problems arise: 1) the difficulty of balancing both pressure transducers as the sampling time increases (use of a pressure transducer with a broad measurement range limits the sensitivity); 2) the difficulty of maintaining a leak-free system increases (a small leak in the system will cause errors in mass measurement).

Only those particles depositing at the entrances to, or inside of the pores of, a filter can contribute to the increase in pressure drop. Therefore, the flow rate was selected to minimize the impaction of particles on the surface of the filter, and to maximize the diffusion and interception of particles inside of the pores. Other factors important in the selection include: 1) ensuring that the change in pressure drop across N1 can be measured in a reasonably period of time for the typical ambient particle concentration; 2) achieving a pressure drop that is not too high (causing operational problems). A capillary pore filter with 0.2 µm pore size and a face velocity of 5 cm/sec was selected.[18]

Koutrakis et al.[9] have shown that, for the CPMM, the increase in pressure drop of N1 can be calculated by 2T1-T2. One of the assumptions is that the pressure drop of N2 is the same as that of N1. This condition is satisfied when using capillary pore filter of larger pore size (2.0 µm). However, this condition is not satisfied when 0.2 µm capillary pore filters are used, because the pressure drop across a capillary pore filter depends upon the flow rate and pressure at the filter face. Because of the pressure drop across N1 (~70 in. of water), the pressure drop across N2 is only about 85% of that across N1. Generally, the pressure drop across N1, P, can be expressed as,

$$\Delta P = \frac{(1=a)T1\ \ T2}{a}$$

$$a = \frac{\Delta P_{N2}}{\Delta P_{N1}}$$

where T1 and T2 are the pressure differentials recorded by pressure transducer 1 and 2. P_{N1} and P_{N2} are the pressure drop across N1 and N2 at a given flow rate, respectively. For a face velocity of 5 cm/sec, the has a value of 0.85.

As aerosol enters the CPMM-U, it is dried by passing through a diffusion dryer. The flow then splits. On the left path, particles deposit on N1 , causing a increase in flow restriction across N1. Any particle that penetrates N1 will be removed completely by the HEPA filter that is located further down the line. Therefore, the flow restriction of N2 will not change due to particle loading during sampling. On the right path, particles are immediately removed by the HEPA filter. The flow restrictions of both the first and second capillary filters will not change due to particle loading during sampling because: 1) the capacity of the HEPA filter is much larger than that of a capillary filter; and 2) the pressure drop across the HEPA filter is less than one hundredth of that across a capillary pore filter under our experimental conditions. Thus, the increase in flow restriction of HEPA filter is negligible in comparison to that of the capillary pore filter.

As particles deposit on N1, the balance of the system is self-adjusted to accommodate the change in flow restriction of N1. Thus, the pressure drop across the N1 increases and the T1 reading increases. Assuming that the flow rates of both lines are not significantly changed during the period of sampling, the T2 reading also increases. For the calibration of the ultrafine particle mass monitor (CPMM-U) we employed a method using an Ultrafine Condensation Particle Counter and monodisperse particles to calibrate the CPMM-U. The system used is described in a separate paper.[19] The results of the calibration tests for various sizes of monodisperse ultrafine particles are shown in Figure 6.

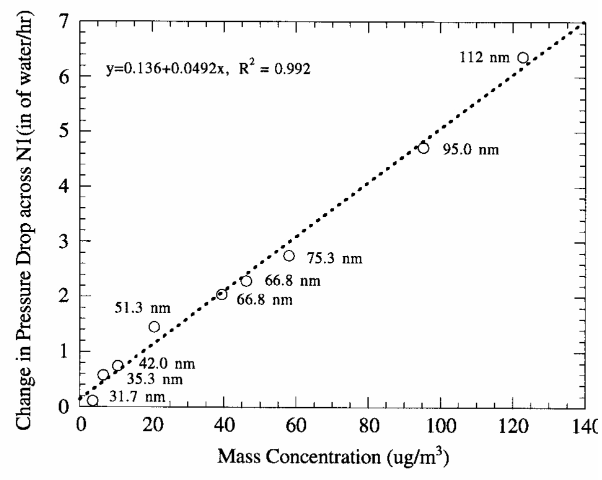


Figure 6. The results of the calibration tests for various sizes of monodisperse ultrafine particles.

Since the pressure drop across the capilliary pore filters in the CPMM-U is 5-7 times higher than that in the CPMM, the filter tape advancement system for CPMM was considered unsuitable for the CPMM-U. Koutrakis et al.[20] have shown that a small leak in the CPMM can cause a significant error in the measurement of mass concentration. To avoid leakage problems we use a multi-head filter holder that can provide a tight seal for each filter. Instead of a filter advancement system, we use a sequential sampling approach. Figure 7 shows the systematic design of the multi-head filter holder. The multi-head filter holder is machined from an aluminum block. Recessed filter holders (the number depends on the optimization of the CPMM-U) are machined into the block. Each filter holder includes a stainless steel screen backup and a gasket. The solenoid valves, which are controlled by a computer, select one sampling channel at a time. The capilliary pore filters are loaded into the filter holder block in the laboratory, and the multi-head filter holder is replaced as a whole in the field. Since the linear range of the instrument extends to a mass concentration up to 20 µg/m^3, one filter may be used for long period sampling if the concentration of particles is relatively low. For example, if the mass concentration of the ultrafine fraction is 1 µg/m^3, the linear response range will not be exceeded until 20 one-hour consecutive samplings are made on one filter. Therefore, a multi-head holder containing 14 filter holders should be sufficient for a one week sampling under almost all ambient conditions in the U.S.

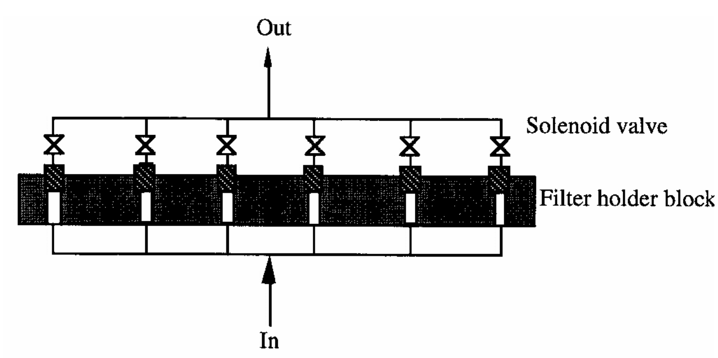
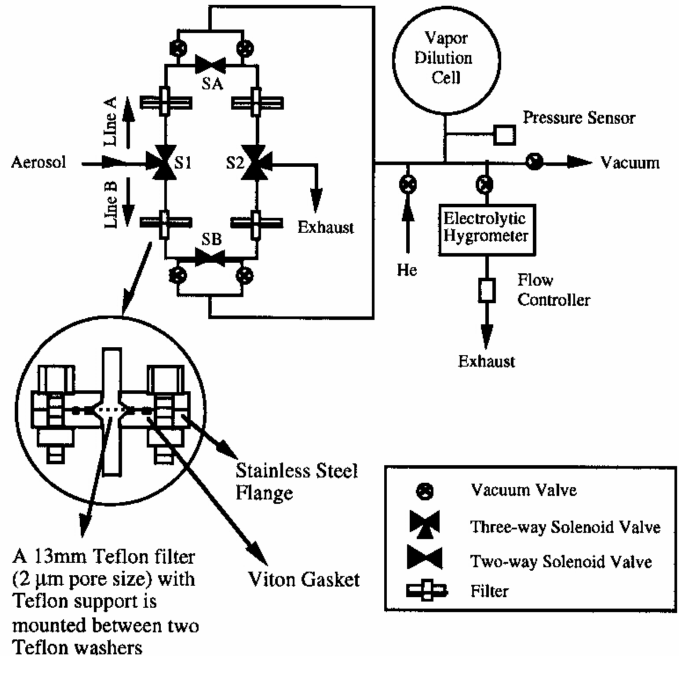


Figure 7. Systematic design of the multi-head filter holder.

2) Particle-Bound Water Detection System: The basic problem that must be overcome is the extremely high background water vapor concentration in the air compared to the water bound by particles at normal environmental conditions. Due to the rapid equilibrium between water vapor and particle surface water (milliseconds time-scale), there is no conventional method for separating the particle-bound water and its coexisting vapor without disturbing the phase equilibrium. The innovative concepts of our method are: 1) to collect particles over a relatively short time period (compared with the time scale of environmental variation); and 2) to collect the particles without disturbing the water equilibrium between the particle and gas phases (by maintaining the sampling system at the condition of the ambient environment); and 3) to minimize the sample cell volume in which the associated air remains. The particle-bound water can then be readily detected above the background in air by means of a highly sensitive moisture detector, such as a P_2O_5-Pt electrolytic hygrometer. The electrolytic hygrometer was chosen as a water detector because: 1) it has the lowest detection limits currently available; 2) it is relatively inexpensive; and 3) it is convenient to operate.



A schematic diagram of our semi-realtime analyzer for particle-bound water in accumulation mode aerosol is illustrated in Figure 8. The basis for the technique is the accretion of PM$_{2.5}$-PM$_{0.15}$ particles by means of a filter over a preset period of time. Two identical sample cells, each one consisting of a 13 mm Teflon membrane filter (2 µm pore size) and a small enclosure, are connected in series. The Teflon membrane filter was selected due to its excellent particle collection efficiency, low moisture uptake, and low trace background. The upstream sample cell collects and preconcentrates the particles in the sampled air from the 0.15 µm virtual impactor, while the second cell analyzes the backgrounds from the air and filter.

Figure 8. Schematic diagram of the system for continuous measurement of particle-bound water within PM$_{2.5}$

A pair of parallel sampling lines are used for alternating the sampling and analysis processes. They are controlled by

2 three-way solenoid valves, the sample inlet valve (S1) and the exhaust valve (S2). When S1 and S2 switch to line A, the line A starts sampling and the line B starts analysis of the samples collected in the prior sampling period. At the end of the sampling period, both S1 and S2 switch, and the functions are reversed. During Line A sampling, solenoid valve SA opens. When switched to analysis, SA closes, and the two sample cells will be separated and analyzed in order. The air background goes first and the aerosol sample next. All the solenoid valves are controlled by an interfacing computer with a preset program.

The water detector consists of a 1000 cm^3 Vapor Dilution Cell (VDC), an Electrolytic Hygrometer, a flow controller, a pressure sensor, a vacuum line, and a helium gas line. The procedures for analysis of the water contents collected by each sample cell are: 1) evacuate the VDC; 2) close the vacuum line and open the VDC to the cell to be analyzed; 3) extract the water bound in the particles and absorbed on the filter and draw it into the VDC along with the air remaining in the cell by vacuum; 4) fill the system with helium gas to a pressure of about 900 torr (slightly higher than atmosphere); 5) open the system to the hygrometer, and allow a small flow (10 cm^3/min) to pass through the electrolytic sensor; and 6) start one measurement. The output signal is recorded and processed by an interfacing data acquisition system. The particle-bound water is determined from the difference between the measurements of the two cells. The filter of the aerosol sample cell is changed after each run.

A P_2O_5-Pt electrode is used to sense water vapor concentration in the system. It consists of a quartz tube wound with two platinum (Pt) wires. The winding is coated with a phosphorus pentoxide (P_2O_5) film, which has a high affinity for H_2O. A voltage is applied to the platinum winding so that the water molecules adsorbed on the P_2O_5 film are electrolyzed to H_2 and O_2 and a current flow is generated as described below:

Cathode reaction:	$2\ H_2O + 2e^- \rightarrow 2\ OH^- + H_2$
Anode reaction:	$2\ OH^- \rightarrow H_2O + \frac{1}{2}\ O_2 + 2\ e^-$

Since every H_2O molecule electrolyzed produces two electrons (based on Faraday's Law of Electrolysis) the current is directly proportional to the concentration of the H_2O molecules in the gas stream. This correlation is insensitive to gas pressure and mass flowrate. The sensor is commercially available for sampling moisture in gas streams and at normal atmospheric pressure. The working range is 0-1000 ppm with an accuracy of 2%. The lowest reported detection limit is 10 ppb.[21] The sample cell volume is 2 cm^3 (See Figure 8). For a flowrate of 1.8 lpm and a sampling time of 60 minutes, the concentration of particle-bound water is elevated by a factor of 5.4×10^5 in relation to its carrier air stream (including a preconcentration factor of 10 provided by the 0.15 virtual impactor). Therefore, the particle-bound water is measured despite the associated vapor in the air stream. A detection limit of the system for measuring particle-bound water is ~5 µg/m^3 of total particle mass concentration with a water composition of 15% at RH above 40%, and 5% at RH below 40%, in a sampling period of 60 minutes.

3) <u>Tungstic Acid Technique - Chemiluminescent NO_x Detector (TAT-CLD) System for Measurements of Particulate Nitrate (NO_3^-) and Ammonium (NH_4^+):</u> A system for continuous measurement of particulate NO_3^- and NH_4^+ is shown in Figure 9. The system combines a two-channel chemiluminescent NOx Analyzer (Monitor Labs, Model 8840) with the Tungstic Acid Technique (TAT) developed by Braman et al.[22] The TAT was used by Braman et al.[22] for preconcentration and determination of gaseous and particulate nitrate and ammonia, based on the principle that nitrate and ammonia are quantitatively chemisorbed at the tungstic acid-coated surfaces at room temperature, and thermally desorbed at high temperature (350°C).

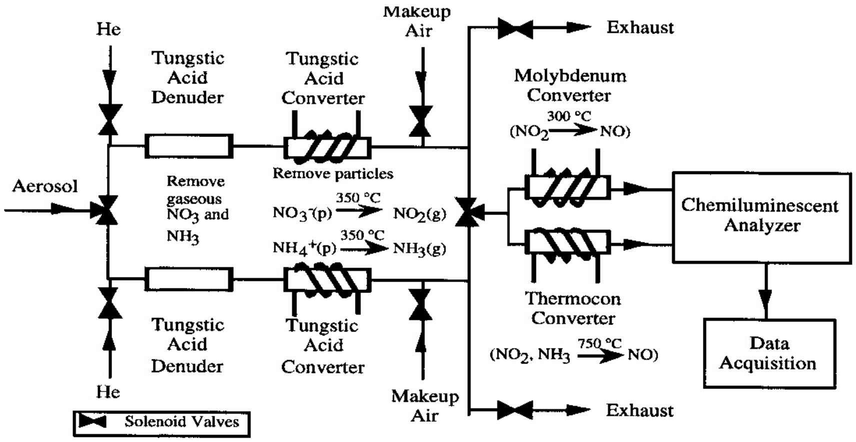


Figure 9. Schematic diagram of tungstic acid denuder and converter-chemiluminescent NO_x detector system for continuous measurement of nitrate and ammonium concentrations in accumulation mode particles.

The advantage of the TAT is that there is essentially no interference of aseous NO_x in either the NO_3^- or NH_4^+ analyses. The weakness of the Braman et al.[22] TAT is the limited particle collection efficiency of the TAF. For a 34 cm long three-section TAF, the particle penetration was as high as 22% at a sampling flowrate of 1 lpM.[22] Large packed tubes can be used to improve efficiency, but this limits the sampling flowrate attainable. In our system, the sample air is preconcentrated 10 times prior to entering the analysis system. The sampling flowrate of the TAT-CLD may be as low as 0.1 - 0.2 lpm without increasing the detection limit of the original TAT. Thus a much higher particle collection efficiency is achieved. A two-channel CLD is used for parallel detection of NO_3^- and NH_4^+ in our system, which simplifies the processes of sample separation. It also minimizes the sampling artifacts reported by Braman et al.[22]

The instrument detection limit of CLD is 2 ppb with a sampling flowrate of 250 ml/min for each channel. The detection limits of TAT-CLD system for ambient accumulation mode particulate NO_3^- and NH_4^+ are below 0.1 µg/m^3 for a 30-minute sampling period.

4) <u>Data Acquisition and System Control:</u> To automate the detection system and the data acquisition, we use a computer interfaced data acquisition and instrument control system. As shown in Figure 10, it consists of an IBM-PC computer, an Analog-to-Digital Converter Board (ADC), a four-channel Signal Conditioner, a Digital Interface Board, and a Multichannel Relay Board (MRB). The Signal Conditioner converts the signals from sensors to standard signals (0 - ± 5V, or 0 - ± 10V), which can be accepted by ADC. The signals received from ADC are recorded and stored in the computer at specified intervals. To control the solenoid valves, a MRB and a Digital Interface is used.

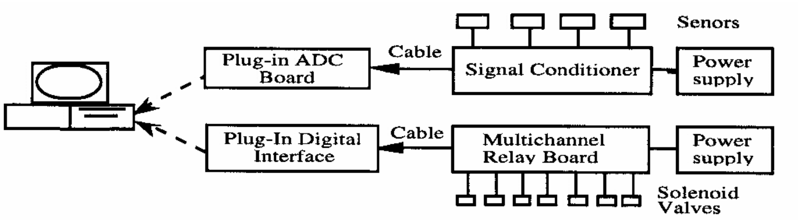


Figure 10. Schematic of the data acquisition and instrument control system.

DISCUSSION

An ambient PM monitoring package (prototype monitor) has been designed to be capable of continuous operation at our laboratories in New York City and in Tuxedo, NY, a location 50 miles north-northwest (NNW) of New York City. It will provide records of concentration data as a fimction of time for PM_{10} and eight of its components, including coarse mode particles (PM_{10}-$PM_{2.5}$), fine particles ($PM_{2.5}$), ultrafine particles ($PM_{0.15}$) and the constituents of the accumulation mode aerosol ($PM_{2.5}$-$PM_{0.15}$) of primary interest, including $SO_4^=$, NO_3^-, NH_4^+, H^+, H_2O, OC, and EC. Using three different pore sizes for the three mass fractions helps insure that interception will be the dominant collection mechanism and that each fraction will be collected within the optimum range for linear response. Using this monitoring system, researchers will be able to measure the mass concentrations of PM_{10} and $PM_{2.5}$ in near real-time, and without sampling artifacts due to sample volatilization and particle-bound water. They will also be able to develop data bases for the concentrations of specific components of $PM_{2.5}$ that may be causal factors for the PM-associated health effects of concern (e.g., H^+, $SO_4^=$, OC, EC, and ultrafines), thereby providing opportunities for more definitive epidemiological studies. Such studies could provide the basis for future NAAQS for specific PM components and thereby more rationale design and implementation of source controls of PM and/or PM precursors.

ACKNOWLEDGMENTS

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The consultation and support of Dr. Petros Koutrakis and his colleagues for our application of the filter resistance method for PM mass concentration measurement developed at the Harvard School of Public Health is also gratefully acknowledged.

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A REAL-TIME SAMPLER RAMS, FOR THE DETERMINATION OF PM$_{2.5}$, INCLUDING SEMI-VOLATILE SPECIES

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The RAMS, Figure 1, is a real-time ambient monitor for the determination of fine particulate mass, including the volatile components (Eatough 1998). The RAMS has a particle concentrator, followed by diffusion denuders to remove gas phase compounds which can be absorbed by charcoal, a Nafion dryer to remove water, and a "sandwich filter" containing a Teflon coated filter to collect particles and a charcoal impregnated filter to retain volatile components which can be lost from the particles during sample collection. Semi-volatile fine particulate material retained on the "sandwich filter" include ammonium nitrate and semi-volatile organic compounds. The "sandwich filter" is located at the tip of the tapered oscillating element of a TEOM monitor and mass retained on the "sandwich filter" is measured as a function of time.

The results obtained with the RAMS have been validated by comparison with results obtained from diffusion denuder integrated samples, to determine the mass of fine particulate material retained on a filter and the semi-volatile organic material and ammonium nitrate lost torn the filter during sampling. This has included comparisons with sampling periods for the denuder samplers as short as 1 hour. Results obtained with RAMS and denuder samplers for samples collected in Riverside CA in the summer and Bakersfield, CA in the winter show that semi-volatile fine particulate species are accurately monitored with the RAMS.

Research is currently underway to validate the measurement of volatile constituents of fine particles with the RAMS in chamber experiments using well characterized particles of ammonium sulfate, ammonium nitrate, glycerol and a carboxylic acid.

ACKNOWLEDGMENTS

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DYNAMIC NUCLEAR POLARIZATION (DNP): A NEW DETECTOR FOR ANALYSIS OF ENVIRONMENTAL TOXICANTS

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The objective of this study is the development of a new analytical instrument designed for environmental monitoring applications. Specifically, this will consist of dynamic nuclear polarization detection with either direct-coupling continuous-flow supercritical fluid chromatography (SFC/DNP) or recycled-flow ^{13}C (DNP) analysis of toxicant mixtures. The DNP detector is a variant of the well known nuclear magnetic resonance (NMR) phenomena. A salient feature of NMR is the chemical shift parameter which provides a very sensitive probe of the local electronic environment about a given atom in a molecule. Thus, the DNP detector could have wide ranging applications for specific monitoring of various organic toxicants mixtures (e.g., chlorocarbons, organophosphates, pesticides, petroleum pollutants, etc.). A major limitation of NMR for most environmental monitoring applications has been sensitivity constraints. The DNP approach helps alleviate the sensitivity limitation of NMR by transfer of polarization from an electron spin to the nuclear spin of interest (^{1}H, $_{13}$C, ^{31}P, etc.). The corresponding DNP signal enhancements are proportional to the electron-to-nuclear magnetogyric ratio (g_B/g_n) which is on the order of 10^3-10^4 for most nuclides.

In this presentation, LC/DNP and SFC/DNP results for chlorocarbon mixtures will be presented, In addition, the results for continuous monitoring of a mixture of benzene and several chlorocarbons with a recycled-flow ^{13}C DNP instrument will also be presented. Finally, progress towards development of a routine SFC/DNP instrument will be reported.

PARTITIONING TRACERS FOR IN-SITU DETECTION AND MEASUREMENT OF NONAQUEOUS LIQUIDS IN POROUS MEDIA

Brusseau

ABSTRACT NOT AVAILABLE

QUALITY ASSURANCE

CD-R ARCHIVE AND CATALOG OF HEWLETT-PACKARD LOW RESOLUTION FORMAT DATA FROM NETWORKED GC/MS SYSTEMS

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ABSTRACT

(1) Taped GC/MS data are not efficiently accessible; (2) Cataloging of archived data with descriptive information requires retyping information entered by the operator at the time of data acquisition. We have addressed these two problems, in our laboratory by archiving all of our data, generated on various Hewlett-Packard GC/MS systems, on CD-R (Compact Disk, Recordable) media. Data are initially sent to a Mylex Level 5 RAID array; then a CD is prepared using the Pinnacle Computing RCD-202 and associated RCD-PC software. A Microsoft Visual Basic program developed in-house (Arch-CD) extracts sample information entered at analysis time from each data file selected for archive and generates a Microsoft Access database (.MDB) file. This MDB file is included with the data files on the CD and also merged with an integrated database. The database along with the CDs on a changer provide instant access to five years of GC/MS data.

INTRODUCTION

Our laboratory applies EPA CLP (Contract Laboratory Protocol) volatilcs and semivolatiles methodology to water and soil samples or their extracts.

- We have four GC/MS systems dedicated to this work, three Hewlett Packard MSD systems and one Varian Saturn Ion Trap system.
- Submission rate for samples of all types averages a modest 750 per year. With daily calibration and other QC, which proceeds irrespective of sample submission, this translates to about 3000 GC/MS runs per year. The average input rate belies the fact that submission is episodic (figure 1) and that samples for a given instrument are received at a rate up to 30 per day, rather than the more prosaic one per day. Turnaround requirements cannot be adjusted to sample submission rate so we must be ready to handle the maximum.
- Prior to 1993, we were limited in disk space, even with a network of PCs, and data was archived on tape. In a major project where non-target analytes are of concern, it is desirable to reevaluate previously processed samples when a new class of substances is detected. The report time is inordinately extended because of the need to move data in and out of storage. Taped GC/MS data are not efficiently viewed or accessed.
- Once data are sent to long-term archive, key information should be put in a database to facilitate future access. A catalog of archived data should contain, at minimum, the descriptive information entered by the operator at the time of data acquisition, but retyping this information into a database is tedious and should be unnecessary.

SUMMARY

We have addressed these two problems of short-term data access and long-term accessibility in our laboratory. For five years we have been archiving all of our data, generated on various Hewlett-Packard GC/MS systems, on CD-R (Compact Disk, Recordable).

- Data are initially sent to a 1.2 Gigabyte partition on a Mylex Level 5 RAID array.
- Then they are mastered using RCD-PC software for the Pinnacle Computing RCD-202 onto a 0.8 Gigabyte partition on the RAID array.
- CD-R disks are prepared and transferred to SCSI chained Pioneer 604X/624X six disk changers.
- CDs beyond the twelve accessible disks are kept in 6-disk cartridges for insertion in the changer and reasonably rapid access.
- A Microsoft Visual Basic program developed in-house (Arch-CD) extracts sample information entered at analysis time from each data file selected for archive and generates a Microsoft Access database (.MDB) file. This is included with the data files on the CD.
- A master database is built up from individual MDB format files.
- The success of this system is illustrated for analysis of volatile organics in water (figure 2). Although the percentage of total time from sample receipt to the analytical report dedicated to data processing has remained a constant 80% - 90%, the total time necessary for analysis and report has fallen significantly since

implementation of this system, from 40 days (or more) to 10 -20 days. During this time, the rate of submission for samples in this category actually increased (figure 1).

- The long report time events of 1995 (figure 2) were due to data glut on our ion trap system, one of the two systems used for water volatiles. This low-level ion-trap system was only recently connected to the network, has limited hard disk storage and has depended on tape backup. We have avoided recurrence of this problem by networking the instrument and archiving its data with those from the HP systems. We have not yet developed information-extraction methodology to incorporate these Saturn data into the database. Hewlett Packard publishes the structure of data files for users whereas Varian does not.

CONCLUSION

Accumulated sample information from a five-year-period is now accessible for HP systems and the data files are readily retrieved for use.

THE USE OF ACCEPTABLE KNOWLEDGE FOR THE CHARACTERIZATION OF TRANSURANIC WASTE IN THE DEPARTMENT OF ENERGY COMPLEX

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ABSTRACT

The Resource Conservation and Recovery Act (RCRA) regulations codified in 40 CFR Parts 260 through 265, 268, and 270, authorize the use of acceptable knowledge as a method which can be used in appropriate circumstances by waste generators, or treatment, storage, or disposal facilities to make hazardous waste determinations. Acceptable knowledge, as an alternative to sampling and analysis, can be used to meet all or part of waste characterization requirements under RCRA.

One example of the use of acceptable knowledge within the U. S. Department of Energy (DOE) complex is the waste characterization requirements for the Waste Isolation Pilot Plant (WIPP), a deep geologic repository for the disposal of transuranic (TRU) waste. The WIPP will be disposing of TRU mixed and non-mixed waste from various generators within the DOE complex in accordance with the provisions of the DOE Carlsbad Area Office (CAO) Quality Assurance Program Plan, the EPA Final Certification Decision, an anticipated RCRA Permit, and the WIPP Waste Acceptance Criteria. Part B of the WIPP RCRA Permit application contains a Waste Analysis Plan which describes the measures that will be taken by the DOE/CAO to assure that mixed wastes received at the WIPP repository are characterized appropriately. To satisfy the characterization requirements, acceptable knowledge is confirmed by radiography, drum headspace gas sampling and analysis, and solidified waste sampling and analysis. Acceptable knowledge is primarily used in TRU waste characterization activities to delineate TRU waste streams, to determine if TRU debris wastes exhibit a toxicity characteristic (40 CFR 261.24), and to determine if TRU wastes are listed (40 CFR 261.31). The physical form and the increased health and safety risks associated with obtaining a representative sample of TRU debris wastes, clearly justify the use of acceptable knowledge in making hazardous waste determinations.

DOE complex waste generators apply knowledge of their waste based on the materials and processes used to generate the waste. Acceptable knowledge includes information regarding the physical form of the waste, the base materials composing the waste, the nature of the radioactivity present, and the process(es) generating the waste.

The DOE/CAO audits the TRU waste generators to grant TRU waste certification authority to the generators. The DOE/CAO conducts audits at least annually thereafter to verify ongoing compliance with approved plans and procedures including those for waste characterization using acceptable knowledge. The information resulting from

DOE/CAO audits is used by the DOE/CAO to help sites across the DOE complex prevent or solve problems associated with the compilation and use of acceptable knowledge for TRU waste characterization. Past and current issues with respect to the compilation, use, and defensibility of acceptable knowledge for TRU waste characterization along with the solutions to those problems and their prevention will be addressed.

INTRODUCTION

Waste Isolation Pilot Plant (WIPP)

The WIPP is a deep geologic repository designed to permanently dispose of transuranic (TRU) radioactive waste generated from the research, development, and production of nuclear weapons in an evaporite salt formation. The mission of the WIPP Project, as authorized by the U.S. Congress in 1979 (Public Law 96-164), is to provide a research and development facility to demonstrate the safe disposal of TRU waste generated as a result of United States defense activities. WIPP is located in Eddy County in southeastern New Mexico about 26 miles east of Carlsbad, New Mexico, in an area known as Los Medanos - a relatively flat, sparsely inhabited plateau with little surface water. WIPP encompasses a 16-square mile area under the jurisdiction of the U.S. Department of Energy (DOE) pursuant to the Land Withdrawal Act.[1] The site boundary was established to ensure that at least 1 mile of intact salt exists laterally between the waste disposal area and the accessible environment and to ensure that no permanent residences will be established in close proximity to the facility.

The DOE's objective is to operate and maintain the WIPP free of both chemical and radiological contamination. Therefore, all waste sampling and analyses will be conducted by the DOE generator/storage sites in accordance with the requirements of the WIPP Waste Analysis Plan (WAP, Chapter C of the RCRA Part B Permit Application)[2] and the WIPP Compliance Certification Application (Chapter 4)[3] as allowed by 20 New Mexico Administrative Code (NMAC) 4.1, Subpart V, Paragraph 264.13, and consistent with joint U.S. Environmental Protection Agency (EPA) and U.S. Nuclear Regulatory Commission guidance.

Transuranic Waste

The transuranic (TRU) elements have atomic numbers greater than that of uranium (92). Examples of transuranic elements include neptunium (Np), plutonium (Pu), americium (Am), curium (Cm), etc. Each element typically has several isotopes and is produced during nuclear reactions. These man-made elements are radioactive and provide the key components for building nuclear weapons.

Transuranic waste consists of clothing, tools, rags, and other items contaminated with trace amounts of radioactive TRU elements - mostly plutonium. TRU waste is defined[1] as "waste containing more than 100 nanocuries of alpha-emitting transuranic isotopes, per gram of waste, with half-lives greater than 20 years, except for a) high-level radioactive waste, b) waste that the Secretary has determined, with concurrence of the Administrator, does not need the degree of isolation required by the disposal regulations; or c) waste that the Nuclear Regulatory Commission has approved for disposal on a case-by-case basis in accordance with Part 61 of Title 10, Code of Federal Regulations."

TRU-mixed waste is waste that is commingled with hazardous materials, such as lead or organic solvents. It is regulated by both the Atomic Energy Act and RCRA (as defined in 20 NMAC 4.1, Subpart VIII, Paragraph 268.35(d) and in the Federal Facility Compliance Act.[4] TRU-mixed waste has physical and radiological characteristics similar to TRU waste. The majority of TRU-mixed waste contains relatively small quantities of spent halogenated solvents, which were used in cleaning and degreasing of equipment, glassware, and components. Based on sampling of gases within TRU waste drums, the most common volatile organic hazardous constituents are methylene chloride, carbon tetrachloride, and 1,1,1-trichloroethane.[5] TRU-mixed waste also contains various RCRA-regulated metals. These metals are usually associated with solid materials, such as lead shielding. Lead, chromium, and cadmium are the most prevalent hazardous metals in TRU-mixed waste. TRU-mixed waste constitutes approximately 60 percent of the DOE's TRU waste.[6] The hazardous components of TRU-mixed waste to be managed at the WIPP are designated in Part A of the RCRA Permit application.[2] Henceforth, the term TRU waste used in this paper includes both TRU and TRU-mixed waste.

Transuranic Waste Generator/Storage Sites

TRU waste has accumulated over the past 50 years as a result of weapons development and production at U.S. defense facilities. Since 1970, DOE has segregated TRU waste from other radioactive waste and stored it in a manner that allows it to be retrieved. TRU waste to be emplaced at WIPP has resulted primarily from the following: (1) nuclear weapons development and manufacturing, (2) plutonium recovery, (3) defense research and development, (4) environmental restoration, (5) decontamination and decommissioning, (6) waste management, and (7) testing at facilities that are under DOE contract.

Table 1 has been reproduced from the National TRU Waste Management Plan.[7] It lists the volumes of TRU waste currently in storage and the volumes of TRU waste projected to be generated by ongoing and new missions during the life of the WIPP. Estimates from environmental restoration, decontamination and decommissioning and future missions are also included. The nuclear weapons complex consists of ten major facilities, including those at large reservations listed in the upper half of Table 1.

Table 1. TRU Waste Storage Locations and Pre-treatment Volumes (cubic meters)[7]

		Contact-Handled TRU Waste		**Remote-Handled TRU Waste**	
Site	**Location**	**Stored***	**Projected through 2033****	**Stored***	**Projected through 2033****
Argonne National Lab.-East	Argonne,IL	94	109	0	0
Hanford Reservation	Richland, WA	16,127	7,305	200	1,592
Idaho National Engineering and Environmental Lab.	Idaho Falls, ID	64,575	15,009	86	53
Lawrence Livermore National Lab.	Livermore, CA	297	835	0	0
Los Alamos National Lab.	Los Alamos, NM	8,255	8,544	101	128
Mound Plant	Miamisburg, OH	241	6	0	0
Nevada Test Site	Nevada	618	19	0	0
Oak Ridge National Lab.	Oak Ridge, TN	917	180	1,268	100
Rocky Flats Environmental Technology Site	Golden, CO	1,505	6,988	1,268	100
Savannah River Site	Aiken, SC	11,725	17,811	1	21
Small-Quantity Sites					
Ames Laboratory	Ames, IA	0	<1	0	0
ARCO *Medical Products Company*	West Chester, PA	<1	<1	0	0
Babcock & Wilcox-NES	Lynchberg, VA	20	0	0	0
Battelle Columbus Laboratories	Columbus, OH	0	0	0	369
Bettis Atomic Power Laboratory	West Mifflin, PA	0	114	0	2
Energy Technology Engineering Center	Santa Susana, CA	7	0	0	1
General Electric-Vallecitos Nuclear Center	Pleasanton, CA	6	3	8	5
Knolls Atomic Power Lab.	Niskayuna, NY	0	0	<1	5
Lawrence Berkeley Lab.	Berkeley, CA	<1	4	0	0
Missouri University Research Reactor	Columbia, MO	<1	1	0	0
Paducah Gaseous Diffusion Plant	Paducah, KY	2	0	0	0
Sandia National Laboratories	Albuquerque, NM	7	44	1	3
U.S. Army Material Command	Rock Island, IL	2.5	0	0	0
Total Waste Volumes***		104,400	56,972	1,666	2,268

* Volumes Prior to treatment and repackaging.

** Projected volumes include estimates from environmental restoration, decontamination and decommissioning, and future Departmental missions, for example, the disposition of weapons-useable plutonium at the Savannah River Site. Estimates will change based upon future compliance actions under environmental law.

*** Totals reflect rounding of numbers.

Continued temporary storage of TRU waste at these and other sites across the nation poses potential problems. For example, some of the metal drums used to store TRU waste are showing signs of corrosion, and the contents of these drums eventually will have to be repackaged. Not only would additional storage facilities be needed at the generator/storage sites, but also additional worker exposures to penetrating radiation would occur due to repackaging and inspection of waste containers. New treatment capacity would also be needed because much of the TRU waste is subject to RCRA Land Disposal Restrictions and cannot be placed in or on the land unless it is treated to satisfy those restrictions. Sound environmental practice requires that TRU waste be permanently isolated to prevent human exposure for many generations to come.

TRANSURANIC WASTE CHARACTERIZATION

The process of identifying and classifying the chemical, physical, and radiological constituents of each drum of waste is a critical aspect of waste characterization. TRU waste characterization is a subset of the waste certification process and is based on sampling and analysis combined with acceptable knowledge of each waste stream in accordance with the requirements of the TRU Waste Characterization Quality Assurance Program Plan[8] (QAPP). The QAPP utilizes a performance-based approach to allow individual sites to have the flexibility to employ analytical and examination methods that meet the quality assurance objectives specified in the Waste Analysis Plan (WAP)[2] and implemented by the requirements of the QAPP.

Retrievably stored[i] TRU waste will be characterized by the generator/storage sites as the waste is retrieved. Newly generated[ii] TRU waste will be characterized as it is generated. Waste characterization requirements for retrievably stored and newly generated wastes are slightly different and are discussed in the WAP. Waste characterization activities at the generator/storage sites include the following, although not all of these techniques will be used on each container:

- Acceptable Knowledge: Compilation of documented characterization and/or process knowledge into an auditable record
- Headspace-gas sampling and analysis: Used to determine volatile organic compound (VOC) content of gases in the void volume of the containers
- Sampling and analysis of homogeneous solid waste forms: Used to determine concentrations of hazardous waste constituents and toxicity characteristic contaminants of waste in containers
- Radiography: an x-ray technique used to determine physical contents of containers
- Visual examination: Used to verify radiography results
- Radioassay: Used to identify isotopic inventory and associated activity

The origins of these requirements in the WAP are traceable to applicable regulatory requirements and commitments made to regulatory authorities such as the NMED and the EPA.

NMED Basis for Waste Characterization

The Waste Analysis Plan (WAP), Chapter C of the RCRA Part B Permit Application,[2] describes the measures that will be taken to assure that TRU waste received at the WIPP facility is within the scope of the RCRA permit as established in and with unit-specific requirements of Title 20 of the New Mexico Administrative Code, Chapter 4, Part 1, Subpart V, Paragraph 264.13 (20 NMAC 4.1). The WAP establishes waste characterization requirements that are referenced in the Waste Acceptance Criteria (WAC),[9] the QAPP, and the TRU-waste generator/storage sites Quality Assurance Project Plans (QAPjPs). It includes descriptions of waste parameters, rationale, and characterization methods; waste sampling and analysis strategies; waste shipment screening and verification processes; and a quality assurance (QA)/quality control (QC) program.

The WIPP underground disposal unit is classified as a "miscellaneous unit" subject to regulation under 40 CFR Part 264, Subpart X. Permit applications for miscellaneous units must describe the wastes to be managed and assess the potential environmental impacts associated with the proposed waste management activities. A listing of the EPA Hazardous Waste Numbers that may be associated with the waste to be emplaced in the miscellaneous unit is contained in Part A of the WIPP RCRA Permit Application.[2] This listing was determined by a survey of the generator/storage sites' TRU waste inventories and includes such RCRA-regulated constituents as:

- toxic characteristic contaminants listed in 20 NMAC 4.1, Subpart II, Paragraph 261.24, Table 1 (corresponding to 40 CFR 261, Subpart C, Paragraph 261.24) except for pesticides,

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[i] Retrievably stored waste is defined as waste generated after 1970 and before implementation of the QAPP characterization requirements.

[ii] Newly generated waste is defined as waste generated after implementation of QAPP characterization requirements.

- F-listed solvents (F001, F002, F003, F004, F005, F006, F007, and F009) found in 20 NMAC 4.1, Subpart I, Paragraph 262.31 (corresponding to 40 CFR 261, Subpart D, Paragraph 261.3 1), and
- hazardous constituents included in 20 NMAC 4.1, Subpart H, Paragraph 261, Appendix VII (corresponding to 40 CFR 261, Appendix VIII).

Waste is characterized on a waste stream basis. A waste stream is defined as waste material generated from a single process or from an activity that is similar in material, physical form, and hazardous constituents. Wastes are initially categorized into three broad Summary Category Groups that are related to the final physical form of the wastes. These groups include homogeneous solids (Summary Category S3000), soil/gravel (Summary Category S4000), and debris wastes (Summary Category S5000). Waste streams are grouped by Waste Matrix Code Groups related to the physical and chemical properties of the waste. Generator/storage sites must use the characterization techniques described in the WAP to assign appropriate Waste Matrix Code Groups for WIPP disposal. The Waste Matrix Code Groups are solidified inorganics, solidified organics, salt waste, soils, lead/cadmium metal, inorganic nonmetal waste, combustible waste, graphite, filters, heterogeneous debris waste, and uncategorized metal.

A statistically selected portion of waste containers from waste streams of homogeneous solids and soil/gravel will be sampled and analyzed for total volatile organic carbons (VOCs), semi-volatile organic compounds (SVOCs), and metals. TRU waste classified as debris wastes will be characterized based on acceptable knowledge. Acceptable knowledge refers to applying knowledge of the hazardous characteristic of the waste in light of the materials or processes used to generate the waste. The use of acceptable knowledge is outlined in a guidance manual[10] wherein the EPA has specifically referred to the characterization of radioactive mixed waste as a situation where the use of acceptable knowledge is appropriate.

Since waste containers will not be opened to perform confirmatory sampling at the WIPP site, waste characterization data produced at the site is reviewed at three levels to ensure it meets Program needs and objectives. At the data generation level, data are reviewed, validated, and verified. Data packages are submitted to the project level for validation and verification. The third and final level is the CAO level at which data from the project level are verified.

Data review determines if the raw data have been properly collected and ensures raw data are properly reduced. Data validation confirms that the data reported satisfy the requirements defined by the user (e.g., quality assurance objectives and data quality objectives) and is accompanied by signature release. Validation at each level ensures that certain aspects of characterization and quality assurance have been met. Data verification authenticates that data are in fact that which is claimed.

EPA Basis for Waste Characterization

An estimate of each generator/storage site TRU waste inventory was compiled in the TRU Waste Baseline Inventory Report,[11] modeled by the performance assessment,[3] and evaluated using a sensitivity analysis to determine the impact of each waste component on the long term performance of the repository. The results of the sensitivity analysis identified several parameters that must be monitored and tracked to assure the validity of assumptions used in the performance assessment. These parameters are listed in an Appendix to the Compliance Certification Application (CCA)[3] entitled "Waste Component Limits" (WCL). Being that Appendix WCL identifies the radionuclide content of the waste as one of the components to be monitored and tracked, radiological characterization of the waste by radioassay is of concern to the EPA.

ACCEPTABLE KNOWLEDGE

The use of acceptable knowledge is discussed in the EPA document, "Waste Analysis: EPA Guidance Manual for Facilities that Generate, Treat, Store and Dispose of Hazardous Wastes."[10] This document points out that there are situations where it may be appropriate to apply acceptable knowledge to characterize hazardous waste. One of these, which is applicable to the type of waste that will be accepted for disposal in the WIPP, is that the physical nature of the waste does not lend itself to the acquisition of a representative sample. Additionally, the RCRA regulations codified in 40 CFR Parts 260 through 265, 268, and 270, authorize the use of acceptable knowledge as a method which can be used in appropriate circumstances by waste generators, or treatment, storage, or disposal facilities to make hazardous waste determinations. Acceptable knowledge, as an alternative to sampling and analysis, can be used to meet all or part of waste characterization requirements under RCRA.

Acceptable knowledge refers to applying knowledge of the waste based on the materials or processes used to generate the waste. Acceptable knowledge includes information regarding the physical form of the waste, the base materials composing the waste, the nature of the radioactivity present, and the process generating the waste. Acceptable knowledge is used to assign matrix parameter categories and EPA hazardous waste numbers to waste streams and to determine the waste material parameters and radionuclides present in waste streams. The collection and use of acceptable knowledge information applies to both retrievably stored and newly generated waste streams.

To satisfy the characterization requirements of the WAP, acceptable knowledge is confirmed by radiography, drum headspace gas sampling and analysis, and solidified waste sampling and analysis. Acceptable knowledge is primarily used in TRU waste characterization activities to delineate TRU waste streams, to determine if TRU debris wastes exhibit a toxicity characteristic (40 CFR 261.24), and to determine if TRU wastes are listed (40 CFR 261.31). The physical form and the increased health and safety risks associated with obtaining a representative sample of TRU debris wastes, clearly justify the use of acceptable knowledge in making hazardous waste determinations.

DOE complex waste generators apply knowledge of their waste based on the materials and processes used to generate the waste. A generator site can establish the characterization of a waste stream by demonstrating an understanding of the materials which are introduced into the process, and the process(es) which those materials undergo. Understanding the process(es) which a material may undergo is very important, particularly with respect to toxicity characteristic wastes, because some chemical processes may result in a change in concentration of the RCRA constituents. Assignment of F-listed wastes also depends on knowledge of the process that produces the waste. A change in concentration of the RCRA constituents during a process could result in a new waste stream containing constituents with concentrations that are above the regulatory threshold. In the case of certain compounds which may be either listed or toxicity characteristic, the use of acceptable knowledge is the only viable route to determine whether a substance was utilized for its solvent properties or not. If a constituent was used for its solvent properties, the waste stream would be assigned an F code. If the constituent was not utilized for its solvent properties, it would be evaluated for the assignment of a D code, if appropriate.

The Land Withdrawal Act[1] included a number of requirements and restrictions on the wastes that can be disposed of at the WIPP. Among these requirements and restrictions are that the waste be generated by atomic energy defense activities and that it is neither high-level waste nor spent nuclear fuel. DOE can verify compliance with these conditions only through the use of historical information about the processes that generated a particular waste stream. This historical information is a component of the acceptable knowledge record that is assembled and assessed by the waste generators.

Consistency among sites in using acceptable knowledge information to characterize TRU waste involves a three phase process: 1) compiling the minimum acceptable knowledge documentation in an auditable record; 2) confirming acceptable knowledge information using radiography, and headspace gas and solidified waste sampling and analysis; and 3) auditing acceptable knowledge records. The consistent presentation of acceptable knowledge among sites in auditable records will allow WIPP personnel to verify the completeness of acceptable knowledge and determine that the accuracy of acceptable knowledge has been documented for TRU waste characterization during the audit process.

AUDITING ACCEPTABLE KNOWLEDGE RECORDS

The DOE/CAO audits the TRU waste generators to grant TRU waste certification authority to the generators. The DOE/CAO conducts audits at least annually thereafter to verify ongoing compliance with approved plans and procedures including those for waste characterization using acceptable knowledge. The information resulting from DOE/CAO audits is used by the DOE/CAO to help sites across the DOE complex prevent or solve problems associated with the compilation and use of acceptable knowledge for TRU waste characterization. Past and current issues with respect to the compilation, use, and defensibility of acceptable knowledge for TRU waste characterization along with the solutions to those problems and their prevention are addressed in this section.

The Audit Process

CAO conducts an initial audit of each site to evaluate waste stream and program documentation prior to certifying the site for shipment of TRU waste to the WIPP facility. The initial audit establishes a baseline that will be reassessed annually. The audits are used to ensure the consistent compilation, application, and interpretation of acceptable knowledge information throughout the DOE complex and to evaluate the completeness and defensibility of site-specific acceptable knowledge documentation related to hazardous waste determinations.

Acceptable knowledge audit checklists typically include, but are not limited to, the following elements for review during the audit:

- Documentation of the process used to compile, evaluate, and record acceptable knowledge is available and implemented

- Personnel training and qualifications are documented

- All of the required acceptable knowledge documentation has been compiled in an auditable record

- Procedures exist for:
  - assigning EPA hazardous waste numbers to waste streams
  - assigning a matrix parameter category to a waste stream
  - determining waste material parameters present in a waste stream
  - determining the radionuclides present in a waste stream
  - resolving inconsistencies in acceptable knowledge documentation
  - confirming acceptable knowledge information through: a) radiography or visual examination, b) headspace gas sampling and analysis, and c) solidified waste sampling

- Results of other audits of the TRU waste characterization programs at the site are available in site records

Auditors assess all documents associated with the evaluation of the acceptable knowledge documentation for at least one debris waste stream and one solidified waste stream during the audit. For these waste streams, auditors review all procedures and associated processes developed by the site for: documenting the process of compiling acceptable knowledge documentation; correlating information to specific waste inventories; assigning EPA hazardous waste numbers; assigning matrix parameter categories; determining waste material parameters; determining the radionuclides; and identifying, resolving, and documenting discrepancies in acceptable knowledge records. The adequacy of acceptable knowledge procedures and processes is assessed and any discrepancies in procedures are documented in the audit report.

Auditors review the acceptable knowledge documentation for selected waste streams for logic, completeness, and defensibility. The criteria used by auditors to evaluate the logic and defensibility of the acceptable knowledge documentation include completeness and traceability of the information, clarity of presentation, degree of compliance with the requirements of the QAPP and WAP with regard to acceptable knowledge confirmation data, nonconformance procedures, and oversight procedures. Auditors evaluate compliance with written site procedures for developing the acceptable knowledge record. A completeness review is done to evaluate the availability of the minimum required TRU waste management and TRU waste stream information. Records are reviewed to assess the correlations to specific waste streams and to assess the basis for making waste determinations. Auditors verify that sites include all required information and conservatively assign all potential EPA hazardous waste numbers indicated by the acceptable knowledge records. All deficiencies found in the acceptable knowledge documentation are included in the audit report.

Auditors verify and document that sites use management controls and follow written procedures to make waste determinations for newly generated and retrievably stored wastes. Auditors review procedures used by sites to confirm acceptable knowledge information using radiography or visual examination, headspace gas sampling and analysis, and solidified waste sampling and analysis. Procedures to document changes in acceptable knowledge documentation, EPA hazardous waste number assignments, matrix parameter category assignments, waste material parameter determinations, and radionuclide determinations to specific waste streams are also evaluated.

After the audit is complete, CAO prepares a final audit report that includes all observations and findings identified during the audit. Sites are required to respond to all audit findings and identify corrective actions. If acceptable knowledge procedures do not exist, the minimum required information is not available, or findings of noncompliance associated with waste determinations are identified, CAO will not grant the site characterization and certification authority for the subject waste. Waste stream characterization and certification authority may be revoked or suspended if findings during subsequent annual audits indicate a lack of compliance with approved acceptable knowledge procedures.

Acceptable Knowledge Issues

To date, the Department of Energy, Carlsbad Area Office has certified three generator/storage sites: Los Alamos National Laboratory (September 1997), Rocky Flats Environmental Technology Site (March 1998), and Idaho National Engineering and Environmental Laboratory (April 1998). These sites have undergone initial and final audits of their certification and acceptable knowledge processes and have successfully met all WAP criteria for characterizing their TRU waste via acceptable knowledge. Issues that the audit team encountered during audits of the adequacy, implementation, and effectiveness of the sites' acceptable knowledge procedures/processes are summarized below.

Adequacy

Procedural inadequacy was a common problem encountered by the audit team. The WIPP requires the "proceduralization" of every aspect of the acceptable knowledge process, from compilation and evaluation of the acceptable knowledge documentation, to reconciliation of discrepancies in the documentation, to waste stream designation and assignment of EPA hazardous waste codes. The following procedural inadequacies were noted by the audit team:

- The responsible party(ies) for some tasks identified in the procedures was not specified
- A list of the documents generated as a result of implementing the procedure was not specified
- Proper approvals for procedures were not obtained prior to implementation
- Approvals for procedures were not adequately documented
- Various requirements were omitted from procedures, such as a specification to look for prohibited waste items
- Necessary or required procedure steps, or forms, or references to other related procedures were not specified

Implementation and Effectiveness

If the acceptable knowledge process procedures are adequate and complete, the satisfactory implementation of these procedures results in accurate and defensible characterization of the waste by the generator, i.e. an effective process. When procedures are not implemented correctly, the result is an incorrect determination, or an inability to characterize the waste using acceptable knowledge, or an ineffective process. The audit team noted several deficiencies with respect to the implementation and effectiveness of acceptable knowledge process procedures:

- Various processes, such as that for amending acceptable knowledge records, were not established
- Some procedures did not reflect current practice
- Some procedures were not being property implemented
- The acceptable knowledge documentation was not traceable to source documents the acceptable knowledge documentation was not compiled into an auditable package or record
- Some sites that subcontracted the acceptable knowledge process work did not include requirements for qualification/training of personnel or a requirement to prepare and train the site personnel in the statement of work for the subcontractor
- The required analytical data and/or acceptable knowledge documentation was not available or insufficient to support the conclusions or EPA hazardous waste code assignments
- Retrieval of records (source documents, etc.) was difficult, time consuming, or impossible
- Documentation of training for various acceptable knowledge processes (review of acceptable knowledge documentation, etc.) was non-existent or insufficient
- EPA hazardous waste codes were removed without sufficient documentation that a discrepancy process was followed
- Acceptable knowledge documentation contains statements that are not corroborated by the source documentation

- The process for the assignment of EPA hazardous waste codes was not consistent with QAPP/WAP requirements
- The acceptable knowledge summary report did not list all potential constituents as shown in supporting documentation
- Documentation to justify that the waste was generated as a result of atomic energy defense activities was insufficient
- Acceptable knowledge documentation for radionuclide distribution was not adequate to support radioassay data to confirm the radionuclide inventory and obtain total activity in TRU waste
- The EPA hazardous waste code for a constituent identified in the acceptable knowledge documentation as being present in the waste was not assigned
- Inconsistencies or discrepancies between acceptable knowledge documentation and/or analytical data were not reported (packaging configuration, volume of waste, etc.)

CONCLUSIONS

Acceptable knowledge provides a reasonable and appropriate means to characterize nuclear waste for disposal. Acceptable knowledge is the only route by which certain characterization decisions (e.g. the origin of the waste being from defense activities, the use of solvents) may be made. The DOE and the waste generator sites have developed and implemented an adequate system for the collection, assessment, and utilization of acceptable knowledge for characterizing waste to be disposed of at the Waste Isolation Pilot Plant.

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PERFORMANCE EVALUATION SOIL SAMPLES FOR VOLATILE ORGANIC COMPOUNDS UTILIZING SOLVENT ENCAPSULATION TECHNOLOGY

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Abstract

A mixture of volatile organic compounds (VOCs) was encapsulated and mixed with soil to produce a product suitable for use as a double blind source of VOCs in soil performance evaluation sample. Two independent laboratories analyzed the standard encapsulated VOC/soil mixture for benzene, toluene, ethylbenzene and xylene by using U.S. EPA SW-846 Method 5030 in conjunction with SW-846 Method 8020. One laboratory received the sample as a single blind standard while the other laboratory received the sample as a double blind standard. The percent relative standard deviation (%RSD) for triplicate analyses ranged from 2.4 to 7.7. The lowest %RSD was for meta/para-xylene (2.4%) from the sample analyzed as a double blind sample. Analytical results from these pilot studies indicate that it is possible to prepare standard soil samples contaminated with known amounts of VOCs, which unlike current market technology, will enable soil samples to be submitted to environmental analytical laboratories as a truly blind sample.

Introduction

For most environmental analytical procedures, demonstrating proficiency of an analytical method is accomplished utilizing known spiked samples, blanks, surrogate spikes and appropriate performance evaluation standards. For analysis of volatile organic compounds (VOCs) in soils, the performance evaluation standards are primarily methanolic solutions that contain target analytes and are spiked into a soil sample immediately prior to analysis.

Demand for precise performance evaluation samples for VOCs in soil matrices has stagnated due to lack of sample preparation technology. Current technology for preparing volatile performance evaluation samples utilize solvent spiking procedures[1] or vapor fortification methodologies developed by J. Hewitt[1] of the U.S. Army Cold[2] Regions Research and Engineering Laboratory. Private sector companies typically provide analysts a dilute solution of analytes in a solvent, usually methanol. These methanol solutions are introduced either into the analytical technique (purge and trap or headspace analyses) or placed onto sand[3] (used to simulate soil) immediately prior to instrumental analysis. These practices do not adequately replicate soil sample handling procedures in the analytical laboratory. Liquid standards also inappropriately provide the analysts with an opportunity to analyze the spiking solution.

Although vapor-fortified soils provide a means of examining spiked soils that are analogous to soils isolated from the environment, such standards are difficult to disseminate to analytical laboratories as a double blind quality control standard. An ideal VOCs in soil standard should provide analyte concentrations across the concentration range of 5 µg/kg to 100 µg/g. Vapor fortification methodology can be customized to decrease concentrations below 100 µg/g, but it is less amenable to water soluble analytes such as acetone or 2-butanone and some target analytes are lost due to the varying absorbtivity of vastly differing soil matrixes. Early attempts to spike, homogenize and transfer soil performance standards were unsatisfactory.[4]

To create a true volatiles in soil performance evaluation standard:
1. Volatile target analytes of interest must be unknown to the analyst.
2. Target analytes must be provided to the analyst in the soil matrix.
3. Volatile components must be protected from potential soil biological activity.
4. The standard must be stable over an extended period of time.
5. The target analytes must provide the laboratory with a wide range of VOC concentrations that are accurate and reproducible independent of analytical methodology applied.

In order to meet these specifications, a novel method of spiking native soil samples is required. The objective of this work is to demonstrate that microencapsulated VOCs provide a novel method of spiking soils and offer an improved means of assessing precision and accuracy of VOC analyses of contaminated soils reported by different analytical laboratories.

Experimental

Microcapsules loaded with a VOC mixture (1:1:1 (V/V/V) toluene, p-xylene and ethylbenzene) were formed by complex coacervation[5]. Figure 1 is a diagram of a typical complex coacervation encapsulation protocol. The shell of the microcapsules formed is primarily gelatin cross-linked with glutaraldehyde.

Standard contaminated soil samples were produced by dispersing a known weight of microcapsules loaded with the VOC mixture into a known weight of soil. Dry subsurface soil taken from the Idaho National Engineering and Environmental Laboratory (INEEL) was sieved (60-80 mesh) and mixed with microcapsules to form a uniform soil/microcapsule mixture. Figure 2 shows the steps envisioned for the preparation of a standard performance evaluation soil sample that unitizes microencapsulated VOCs.

VOCs in soil standards were characterized by gas chromatography. A Hewlett Packard 5880 Series II flame ionization gas chromatograph was used. For toluene, ethylbenzene and p-xylene mixture, the column was a 30 meter X 0.53 mm J&W Scientific DB-624 capillary column. For gasoline, the column was a 30 meter X 0.32 mm J&W Scientific DB-1 fused silica capillary column.

In order to analyze the VOC content of capsules and soil containing capsules, a known weight of sample was equilibrated in methanol at room temperature for a finite period. The samples were gently swirled to assure complete wetting of the soil with the solvent. The methanol solution obtained was assayed directly (in the case of gasoline in soil) or diluted with acetone and subsequently assayed (in the case of 1:1:1 toluene/ethylbenzene/p-xylene). Equilibration time was 30 min. for all samples.

Results and Discussion

In order to have a stable standard soil sample contaminated with VOCs, it is necessary to be able to prepare in a reproducible manner VOC-loaded microcapsules that are stable for prolonged periods when mixed with a soil sample. For a microcapsule loaded with VOCs to be stable, the capsule shell or coating must have essentially zero permeability to the VOCs encapsulated. The shell must also be susceptible to water and/or methanol, since the analytical methodology used to characterize VOC contaminated soil involves these solvents. Dry microcapsules shells formed by complex coacervation are able to retain VOCs for prolonged periods as long as they are not subject to high humidity storage conditions. In the presence of water or water/methanol mixtures, the predominately gelatin shells become permeable thereby enabling release of the VOCs.

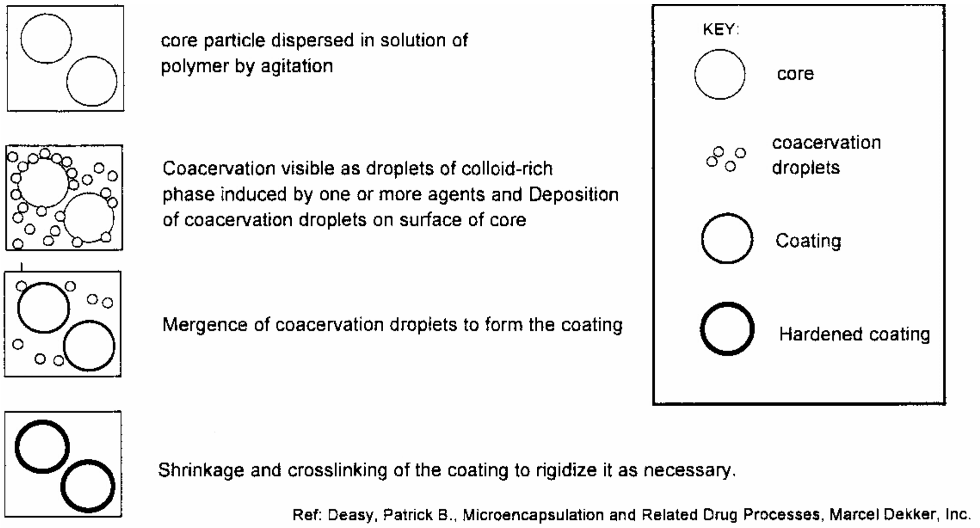
The first objective of the study was to demonstrate that a mixture of pure solvents could be encapsulated and retained. The solvent mixture encapsulated was a 1:1:1 (V/V/V) mixture of toluene, ethylbenzene and p-xylene. Three batches of capsules were made in order to examine lot-to-lot reproducibility. The capsules produced were clean, uniform free-flowing powders suitable for incorporation into a soil sample. Triplicate analyses of 2 gram samples of each capsule batch established that the capsules were 95.8 weight % solvent (relative percent standard deviation; 1.0%). When 5.08 grams of one capsule sample, fraction passing 60 mesh screen, was combined with 100.2 grams clean INEEL subsurface soil, the contaminated soil produced contained approximately 56.5 milligrams (estimated by calculation) of toluene/ethylbenzene/p-xylene mixture per gram of soil.

In order to examine homogeneity and accuracy this standard contaminated soil sample, three one-gram and three five-gram samples of contaminated soil were assayed. Table 1 summarizes the replicate analytical data obtained. Overall variability at one standard deviation was about 5% for all components at either the 1.0 gram or 5.0 gram aliquot size. This single analysis indicates that the concept of preparing an accurate performance standard by utilizing microcapsules is realistic. It demonstrated adequate homogeneity in the sample at various sample sizes as well as relative agreement with the amount of material expected (estimated 56.5 mg/gram vs. found 48.6 mg/gram).

A second pilot involved the encapsulation of gasoline and preparation of soil sample contaminated with gasoline. Four batches of capsules loaded with gasoline were prepared. The mean gasoline loading of these four samples was 73.2% (standard deviation 6.2). Three ~2 gram samples of gasoline-loaded capsules were subjected in triplicate to analysis and found to 3274 µg/gram toluene (std. dev. = 248, %RSD = 7.6), 4347 µg/g ethylbenzene (std. dev. = 296, %RSD = 6.8) and 14922 µg /g p-xylene (std. dev. 931, %RSD = 6.2).

Ten grams of gasoline-loaded capsules were combined with 193.0 grams of soil to produce a pilot performance evaluation sample. Three samples of this contaminated soil sample placed into individual 40 milliliter, precleaned sampling vials each containing approximately 20 grams, were shipped to an environmental analytical laboratory for analysis for benzene, toluene, ethylbenzene and xylenes (BTEX). Each sample was analyzed in triplicate utilizing U.S. EPA SW-846 Method 5030 in conjunction with SW846 Method 8020. Table 2 contains results of these analyses.

Another sample was sent as a double blind sample to a second analytical laboratory for analysis. Table 3) summarizes results of these analyses. Other than a disagreement concerning the quantitation of benzene, results obtained independently by the two laboratories agree well.



Ref: Deasy, Patrick B., Microencapsulation and Related Drug Processes, Marcel Dekker, Inc.

Figure 1. Coacervation of Solvents for Addition to Soil Sample

The analytical data obtained to date demonstrates using microcapsules to prepare soil performance evaluation standards is attainable. The performance evaluation soil standard has the advantage of being as close to a real world soil sample as technologically feasible and has demonstrated the ability to measure the quality associated with the entire analytical methodology. This technology is capable of producing a performance evaluation sample containing volatile target organic analytes within well-defined concentration ranges. The encapsulated process can provide variable concentration ranges for numerous target volatile analytes. The resulting performance evaluation sample will be amenable to many of the current US EPA methodologies for the analysis of environmentally significant volatile organics in soils including analysis carried out by thermal desorption techniques.

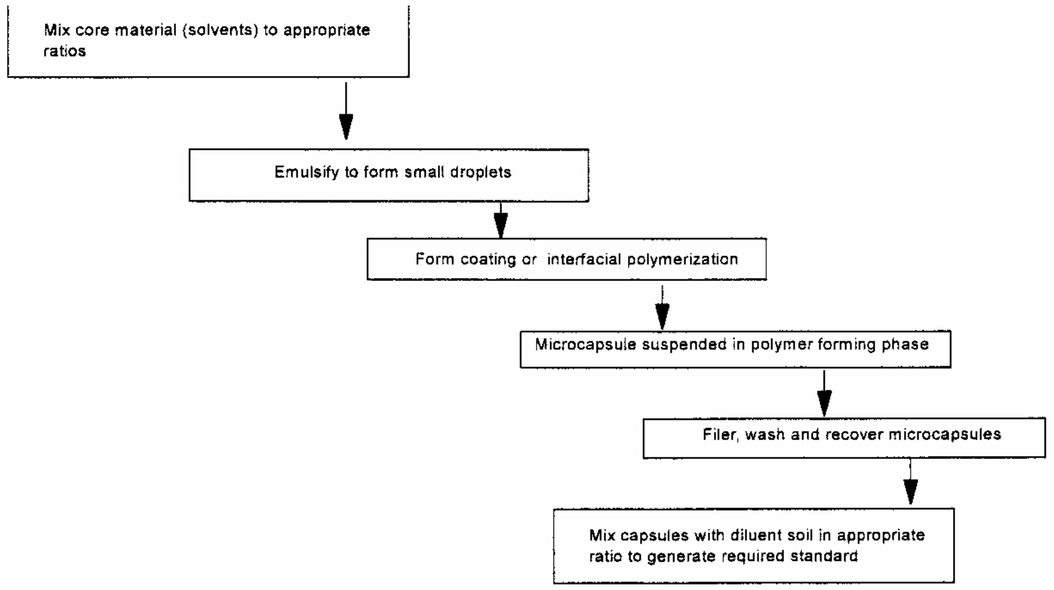


Figure 2. Typical Steps of Standard Preparation Process

Current efforts are focused on reducing the concentration of target analytes to the 5 - 200 ppb range and to examine product storage stability. Once through this pilot examination, the carrier solvent will be spiked with other analytes including; acetone, carbon tetrachloride, chloroform, methylene chloride, trichloroethane, tetrachloroethylene. The author has submitted soil samples that contain microencapsulated VOCs to the Mixed Analyte Performance Evaluation Program, operated by the U.S. Department of Energy, for round robin study utilizing contracted environmental analytical laboratories.

Table 1. Data from Simulated Contaminated Soil Sample that Contains Microcapsules Loaded with a 1:1:1 (V/V/V) Toluene/ Ethylbenzene/p-Xylene Mixture. (units are milligrams per grain of soil)

Sample Weight (g.)		Toluene	Ethylbenzene	p-Xylene
1.0	Average	11.96	22.21	22.41
	Std. Dev.	0.57	1.05	1.08
	%RSD	4.8	4.7	4.8
5.0				
	Average	12.00	22.78	23.02
	Std. Dev.	0.62	1.16	1.17
	%RSD	5.1	5.1	5.1

Table 2. Gasoline in Soil Pilot Performance Evaluation Standard - Single Lab Analysis. (units are milligrams per gram of soil)

	Benzene	Toluene	Ethylbenzene	o-Xylene	m & p-Xylene
Sample 1	444	143	187	341	898
	406	134	206	306	846
	407	130	168	303	841
Sample 2	367	131	192	267	792
	402	130	198	286	793
	416	133	205	280	828
Sample 3	387	131	197	298	814
	384	124	191	261	766
	406	131	200	287	836
Average	402.1	131.9	193.8	292.1	823.8
Std. Dev.	20.5	4.7	10.9	22.5	36.3
%RSD	5.1	3.6	5.6	7.7	4.4

Table 3. Gasoline in Soil Pilot Performance Standard Sent as Double Blind to Second Lab for Analysis. (units are milligrams per gram of soil)

	Benzene	Toluene	Ethylbenzene	o-Xylene	m & p-Xylene
Sample 1	2.5 U	120	150	270	750
	2.5 U	120	150	270	760
	2.5 U	99	120	230	610
	2.5 U	100	110	250	680
Average		109.8	130	255	700
Std. Dev.		10.2	16.7	16.6	60.4
%RSD		9.3	12.9	6.5	8.6
Sample 1	NA	120	200	350	900
Confirmation	NA	120	210	360	940
	NA	120	220	3 80	960
	NA	120	210	350	920
Average		120	210	360	930
Std. Dev.		0	7.1	12.2	22.4
%RSD			3.4	3.4	2.4

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U.S. EPA AND U.S. A.F. INTERAGENCY AGREEMENT FOR FIELD ANALYTICAL SERVICES

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The interagency agreement (IAG) between the parties above will provide for more timely analyses of EPA samples while at the same time making more efficient use of the federal government's resources. At the time of the writing of this abstract the IAG has just reached implementation phase and consequently data is limited. We are confident that with the data generated in the next four months, we will be able to show that time and money are saved by the use of this IAG. As the Project officers for the EPA-AF IAG, we will use the data from each field project in making the cost savings comparison. We will discuss project startup and implementation. The onsite analytical capabilities of the Air Force, both field screening techniques and field confirmation methods, will be examined. USAF's Armstrong Laboratory located at Brooks Air Force Base, San Antonio Texas, will provide onsite analyses for USEPA Region 6's Superfund Division. The elements of the Superfund Program that can request work are the Brownfields, Removal, Emergency Response, Remedial, and Site Assessment Teams. The Air Force Responders will be onsite in a time frame dependent upon the nature of the site activity. Most site activities are non-emergency. Activities which are not time critical such as Brownfields and Remedial for example, will allow sufficient time for a significant amount of preplanning for onsite activities. Other activities which are more time critical require immediate action. Air Force responds to those activities in which there is a threat or possible threat of risk to human health in less than 24 hours dependent on site location. In the near future, AF is projected to have a mobile laboratory which can be driven to the site immediately upon notice.

Onsite field screening and confirmation techniques have been projected to be a more cost effective way to perform portions of the chemical analysis evaluation of a site as early as 1988. Air Force's trained personnel and specialized equipment can be used for EPA projects in EPA Region 6 and of course for Air Force's needs worldwide. Air Force benefits in a number of ways such as becoming familiarized with EPA's SOPs for site activities. EPA benefits by having access to a cost-effective service with unique capabilities and world wide experience. This IAG provides for technology transfer and more efficient resource utilization.

SUMMARY

This agreement between Federal Agencies pursuing common goals allows for greater efficiency and cost effectiveness for all and provides an opportunity for technology transfer. We recommend the use of interagency agreements in similar cases. An IAG can be a commensal relationship with mutual advantages.

SEVERAL ORGANIC PARAMETERS ON UNDERLYING HAZARDOUS CONSTITUENTS LIST CAN NOT BE MEASURED AT THE UNIVERSAL TREATMENT STANDARDS

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ABSTRACT

The Idaho National Engineering and Environmental Laboratory (INEEL) has several permitted treatment, storage and disposal facilities. The INEEL Sample Management Office (SMO), operated by Lockheed Martin Idaho Technologies

Company (LMITCO), conducts all analysis subcontracting activities for Department of Energy Environmental Management programs at the INEEL. In this role, the INEEL SMO has had the opportunity to subcontract the analyses of various wastes (including ash from an interim status incinerator) requesting a target analyte list equivalent to the constituents listed in 40 Code of Federal Regulations (CFR) § 268.48. Per 40 CFR § 268.40, these analyses are required to ensure that treated wastes do not contain underlying hazardous constituents (UHC) at concentrations greater than the universal treatment standards (UTS) prior to land disposal. The language in 40 CFR § 268.40 (d) (3) states that, "The treatment or disposal facility may demonstrate compliance with organic constituents if good-faith analytical efforts achieve detection limits for the regulated organic constituents that do not exceed the treatment standards specified in this section by an order of magnitude."

The INEEL SMO has conducted this "good-faith effort" by negotiating with several commercial laboratories to identify the lowest possible quantitation and detection limits that can be achieved for the organic LTHC analytes. The results of this negotiating effort has been the discovery that no single laboratory (currently under subcontract with the INEEL SMO) can achieve a detection level that is within an order of magnitude of the UTS for all organic parameters on a clean sample matrix (e.g., sand). This indicates that for a typical waste sample, the chances of the order of magnitude requirement not being met for many more than just the "problem analytes" is likely. This does not mean that there is no laboratory that can achieve the order of magnitude requirements for all organic UHCs on a clean sample matrix. The negotiations held to date indicate that it is likely that no laboratory can achieve the order of magnitude requirements for a difficult sample matrix (e.g., an incinerator ash). The authors suggest that the regulation needs to be revised to address the disparity between what is achievable in the laboratory and the regulatory levels required by the UTS.

INTRODUCTION

The INEEL SMO conducts all analysis subcontracting activities for the Department of Energy Environmental Management programs at the INEEL. Contracted analyses are primarily in the following analytical disciplines; radiological, inorganic, organic and physical properties testing. Within each discipline numerous analytical tests are requested on a large variety of sample matrices. Analytical test requirements range from field screening or processing information to data required to satisfy U.S. Environmental Protection Agency (EPA) and Idaho Division of Environmental Quality (ID-DEQ) requirements. The INEEL SMO subcontracts analytical work on a variety of wastes (including ash from an interim status incinerator). Analytical requests have included a target analyte list equivalent to the constituents listed in 40 CFR § 268.48. Per 40 CFR § 268.40, these analyses are required to ensure that treated wastes do not contain UHCs at concentrations greater than the UTS prior to land disposal. The language in 40 CFR § 268.40 (d) states:

> "Notwithstanding the prohibitions specified in paragraph (a) of this section, treatment and disposal facilities may demonstrate (and certify pursuant to 40 CFR § 268.7(b)(5)) compliance with the treatment standards for organic constituents specified by a footnote in the table "Treatment Standards for Hazardous Wastes" in this section, provided the following conditions are satisfied:
> (1) The treatment standards for the organic constituents were established based on incineration in units operated in accordance with the technical requirements of 40 CFR part 264, subpart 0, or based on combustion in fuel substitution units operating in accordance with applicable technical requirements;
> (2) The treatment or disposal facility has used the methods referenced in paragraph (d)(1) of this section to treat the organic constituents; and
> (3) The treatment or disposal facility may demonstrate compliance with organic constituents if good-faith analytical efforts achieve detection limits for the regulated organic constituents that do not exceed the treatment standards specified in this section by an order of magnitude."

The INEEL SMO has sought this "good-faith effort" by negotiating with several commercial laboratories to identify the lowest possible quantitation or detection limits that can be achieved for the organic UHCs. The primary emphasis has been on the nonwastewater standard. At this time, the wastewater standard for the organic UHCs has not been performed by all of the INEEL SMO contracted laboratories. The results of this negotiating effort has been the discovery that no single laboratory (currently under subcontract with the INEEL SMO) can achieve the detection level of the UTS for all organic parameters of the UHC list on a clean sample matrix (e.g., sand). This indicates that for a typical waste sample, the chances of the order of magnitude requirement not being met for many more than just the "problem analytes" is likely. This does not mean that there is no laboratory that can achieve the order of magnitude requirements for all organic UHCs on a clean sample matrix. The INEEL SMO continues to seek laboratory capability to analyze for the UHCs to the UTS in a cost-effective manner. Additionally, the regulated community should be aware that the "order-of-magnitude" provision might not be allowed on incinerator ash from an interim status incinerator. In the September 19, 1994 final rule, the "order-of-magnitude" provision is only applicable where incinerated wastes were treated in permitted (Part 264 Subpart O) units.

Within the capabilities of the current INEEL SMO subcontracted laboratories, no two laboratories analyze the UHCs to the UTS the same way. In the guidelines of USEPA SW-846 a variety of approved methods can be used to analyze for the various constituents. The SW-846 methods being used to analyze for the complete UHC list by the laboratories currently contracted through the INEEL SMO are:

- Method 1311 Toxicity Characteristic Leaching Procedure
- Method 8015A Nonhalogenated Volatile Organics by Gas Chromatography
- Method 8015M (modified) Nonhalogenated Volatile Organics
- Method 8080A Organochlorine Pesticides And Polychlorinated Biphenyls By Gas Chromatography
- Method 8081 Organochlorine Pesticides, Halowaxes And PCBs As Aroclors By Gas Chromatography: Capillary Column Technique
- Method 8081A Organochlorine Pesticides (PCBs) By Gas Chromatography
- Method 8082 Polychlorinated Biphenyls By Gas Chromatography
- Method 8140 Organophosphorus Pesticides
- Method 8141 Organophosphorus Compounds By Gas Chromatography: Capillary Column Technique
- Method 8150 Chlorinated Herbicides By Gas Chromatography
- Method 8151 Chlorinated Herbicides By GC Using Methylation Or Pentafluorobenzylation Derivatization: Capillary Column Technique
- Method 8260A Volatile Organic Compounds By Gas Chromatography Mass Spectrometry (GC/MS): Capillary Column Technique
- Method 8270B Semivolatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique
- Method 8310 Polynuclear Aromatic Hydrocarbons
- Method 8316 Acrylamide, Acrylonitrile And Acrolein By High Performance Liquid Chromatography (HPLC)

The UHC list is extensive and there are many "problem analytes" to analyze. The methodology is left to the capability of the laboratory and the laboratory's discretion. It would not be practical or reasonable for the INEEL SMO to specify to a laboratory a required method for every constituent. Under the fixed contracts, obsolete methods are still listed but current methodology is used whenever possible, incorporating the June 13, 1997 promulgated methods from the Third Edition of the EPA-approved test methods manual "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods."

To procure UHC organic analyses, it becomes necessary to negotiate with each contracted laboratory concerning achievable detection and quantitation limits for the entire UHC list. The negotiations held to date indicate that it is likely that no laboratory can achieve the order of magnitude requirements for a difficult sample matrix (e.g., an incinerator ash). When negotiating with commercial laboratories that are under fixed price subcontracts government contractors like LMITCO have difficulty authorizing additional financial support, for the "research project" samples. Analytical difficulties arise when dealing with complex matrices such as an incinerator fly ash. For example, alternate solvent system extractions may be more effective for the semivolatile organic compounds. Laboratories currently contracted through the INEEL SMO routinely extract semivolatiles using acetone/hexane or acetone/methylene chloride systems. They have found fewer fly ash matrix interferences when they substituted a methylene chloride only extraction system. The alternate solvent system also requires additional calibration with a resulting burden on the laboratory under a fixed price contract.

The organic UHC list is extensive and standards are hard to locate for the entire list. For example, one of the contracted laboratories had difficulty initially procuring a standard for 4,4'-Methylene-bis-(*o*-chloroaniline) CAS# 101-14-4. No laboratory contracted through the INEEL SMO has determined quantitation limits or calibrated for the 40 additional analytes that will become "underlying hazardous constituents" August 26, 1998. Commercial laboratories contracted through the INEEL SMO have expressed concerns about the effort and expense that will be required to obtain standards, conduct MDL determinations, etc. in order to analyze for the added constituents. The 40 additional constituents are identified in Table 1 UTS.

SUMMARY

The current INEEL SMO contracted laboratories operate within the highly competitive commercial laboratory industry. With laboratory capacity available to DOE (i.e. possessing a NRC license to receive radioactively contaminated samples) limited nationwide, extensive "non-routine" analytical requests on complex matrices are not desired by the laboratories. Obtaining the full suite of UHC analyses can be difficult. The inability to determine if a treated waste has achieved the required treatment standard concentrations can place programs in a position subject to violation of regulatory requirements. The authors' suggest that the regulation needs to be revised to address the disparity between what is achievable in the laboratory and the regulatory levels required by the UTS.

The authors' poster delineates the achievable detection limits for organic UHC parameters at several commercial laboratories. The intent of the poster is to bring this issue to the attention of the regulators and regulated community. Another benefit is to discuss analytical approaches used by other laboratories that may achieve greater sensitivities for the difficult organic analytes on the UHC list.

Table 1 UTS identifies the organic hazardous constituents, along with the nonwastewater and wastewater treatment standard levels. 40 CFR § 268.48 also states: "For determining compliance with treatment standards for underlying hazardous constituents as defined in § 268.2(i), these treatment standards may not be exceeded. Compliance with these treatment standards is measured by an analysis of grab samples, unless otherwise noted in the following Table 1 UTS". Included in the table are the negotiated quantitation limits for the nonwastewater standard from three INEEL SMO contracted laboratories (A, B, and C). These limits can be compared to the listed regulatory nonwastewater standard concentration. Presently the most difficult ash samples are requiring five to ten fold dilutions -in addition to alternate solvent system extractions- which further limit the ability of the laboratory to achieve quantitation limits at (or below) the UTS for all of the UHCs. The negotiated quantitation limits are the laboratories "ideal" quantitation limits on a clean matrix (e.g., sand) and do not represent the current achievable limits on difficult sample matrices (e.g., incinerator fly ash). When the laboratories quantitation limit is at the treatment standard concentration, the INEEL SMO requires the laboratory to have the instrument detection limit for that analyte less than 0.33 times the treatment standard. This limit is also specified in the task order statement of work between the laboratory and the INEEL SMO.

Table 1. UTS -- Universal Treatment Standards
(Note: NA means not applicable.)

Regulated constituent/common name Organic Constituents	CAS (1) Number	Wastewater standard Concentration in mg/l (2)	Nonwastewater standard Concentration in mg/kg (3) unless noted as "mg/l TCLP"	Negotiated Nonwastewater Quantitation Limit INEEL SMO contracted Laboratory A	Negotiated Nonwastewater Quantitation Limit INEEL SMO contracted Laboratory B	Negotiated Nonwastewater Quantitation Limit INEEL SMO contracted Laboratory C
A2213 (6)	30558-43-1	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Acenaphthylene	208-96-8	0.059	3.4	0.33	0.67	3.4
Acenapthene	83-32-9	0.059	3.4	0.33	0.67	3.4
Acetone	67-64-1	0.28	160	0.01	0.01	160
Acetonitrile	75-05-8	5.6	38	0.02	0.05	38
Acetophenone	96-86-2	0.010	9.7	0.33	0.67	9.7
2-Acetylaminofluorene	53-96-3	0.059	140	0.33	0.67	140
Acrolein	107-02-8	0.29	NA	0.01	NA	NA
Acrylamide	79-06-1	19	23	**50**	23	23
Acrylonitrile	107-13-1	0.24	84	0.01	0.05	84
Aldicarb sulfuric (6)	1646-88-4	0.056	0.28	**undetermined**	**undetermined**	**undetermined**
Aldrin	309-00-2	0.021	0.066	0.005	0.066	0.066
4-Aminobiphenyl	92-67-1	0.13	NA	0.33	NA	NA
Aniline	62-53-3	0.81	14	0.33	0.67	14
Anthracene	120-12-7	0.059	3.4	0.33	0.67	3.4
Aramite	140-57-8	0.36	NA	0.66	NA	NA
alpha-BHC	319-84-6	0.00014	0.066	0.005	0.002	0.066
beta-BHC	319-85-7	0.00014	0.066	0.005	0.004	0.066
delta-BHC	319-86-8	0.023	0.066	0.005	0.006	0.066
gamma-BHC	58-89-9	0.001	0.066	0.005	0.002	0.066
Barban (6)	101-27-9	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Bendiocarb (6)	22781-23-3	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Bendiocarb phenol (6)	22961-82-6	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Benomyl (6)	17804-35-2	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Benzene	71-43-2	0.14	10	0.005	0.005	10

Benz(a)anthracene	56-55-3	0.059	3.4	0.33	0.67	3.4
Benzal chloride	98-87-3	0.055	6.0	1.65	0.05	6.0
Benzo(b)fluoranthene (difficult to distinguish from benzo(k) fluoranthene	205-99-2	0.11	6.8	0.33	0.67	6 8
Benzo(k)fluoranthene (difficult to distinguish from benzo(b) fluoranthene)	207-08-9	0.11	6.8	0.33	0.67	6.8
Benzo(g,h,i)perylene	191-24-2	0.0055	1.8	0.33	0.67	1.8
Benzo(a)pyrene	50-32-8	0.061	3.4	0.33	0.67	3.4
Bromodichloromethane	75-27-4	0.35	15	0.005	0.05	15
Bromomethane/Methyl bromide	74-83-9	0.11	15	0.01	0.05	15
4-Bromophenyl phenyl ether	101-55-3	0.055	15	0.33	0.67	15
n-Butyl alcohol	71-36-3	5.6	2.6	0.5	2.6	2.6
Butylate (6)	2008-41-5	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Butyl benzyl phthalate	85-68-7	0.017	28	0.33	67	28
2-sec-Butyl-4,6-dinitrophenol/Dinoseb	88-85-7	0.066	2.5	1.65	1.3	2.5
Carbaryl (6)	63-25-2	0.006	0 14	**undetermined**	**undetermined**	**undetermined**
Carbenzadim (6)	10605-21-7	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Carbofuran (6)	1563-66-2	0.006	0 14	**undetermined**	**undetermined**	**undetermined**
Carbodfuran phenol {6}	1563-38-8	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Carbon disulfide	75-15-0	3.8	4.8 mg/l TCLP	.005 mg/l TCLP	4.8 mg/l TCLP	4.8 mg/ TCLP
Carbon tetrachloride	56-23-5	0.057	6.0	0.005	0.005	6.0
Carbosulfan (6)	55285-14-9	0.028	1.4	**undetermined**	**undetermined**	**undetermined**
Chlordane (alpha and gamma isomers)	57-74-9	0.0033	0.26	0.005	0.009	0.26
p-Chloroaniline	106-47-8	0.46	16	0.33	0.67	16
Chlorobenzene	108-90-7	0.057	6.0	0.005	0.005	6.0
Chlorobenzilate	510-15-6	0.10	NA	0.33	NA	NA
2-Cloro-1,3-butadiene	126-99-8	0.057	28	0.01	0.05	0.28
Chlorodibromomethane	124-48-1	0.057	15	0.005	0.005	15
Chloroethane	75-00-3	0.27	6.0	0.01	0.05	6.0
bis(2-chloroethoxy) methane	111-91-1	0.036	7.2	0.33	0.67	7.2
bis(2-Chloroethyl)ether	111-44-4	0.033	6.0	0.33	0.67	6.0
Chloroform	67-66-3	0.046	6.0	0.005	0.005	6.0
bis(2-Chloroisopropyl) ether	39638-32-9	0.055	7.2	0.33	0.67	7.2
p-Chloro-m-cresol	59-50-7	0.018	14	0.33	0.67	14
2-Chloroethylvinyl ether	110-75-8	0.062	NA	0.01	NA	NA
Chloromethane/Methyl chloride	74-87-3	0.19	30	0.01	0.05	30
2-Chloronaphthalene	91-58-7	0.055	5.6	33	0.67	5.6
2-Chlorophenol	95-57-8	0.044	5.7	0.33	0.67	5.7
3-Chloropropylene	107-05-1	0.036	30	0.02	0.05	30
Chrysene	218-01-9	0.059	3.4	0.33	0.67	3.4
o-Cresol	95-48-7	0.11	5.6	0.33	0.67	5.6
m-Cresol (difficult to distinguish from p-cresol)	108-39-4	0.77	5.6	Reported as p-cresol	Reported as p-cresol	Reported as p-cresol
p-Cresol (difficult to distinguish from m-cresol)	106-44-5	0.77	5.6	0.33	0.67	5.6
m-Cumenyl methylcarbamate (6)	64-00-6	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Cyclohexanone	108-94-1	0.36	0.75 mg/l TCLP	0.1 mg/l TCLP	0.75 mg/l TCLP	0.75 mg/l TCLP
o,p'-DDD	53-19-0	0.023	0.087	0.01	0.087	0.087
p,p'-DDD	72-54-8	0.023	0.087	0.01	0.087	0.087
o,p'-DDE	3424-82-6	0.031	0.087	0.01	0.087	0.087
p,p'-DDE	72-55-9	0.031	0.087	0.01	0.087	0.087
o,p'-DDT	789-02-6	0.0039	0.087	0.01	0.087	0.087
p,p'-DDT	50-29-3	0.0039	0.087	0.01	0.087	0.087
Dibenz(a,h)anthracene	53-70-3	0.055	8.2	0.33	0.67	8.2
Dibenz(a,e)pyrene	192-65-4	0.061	NA	0.01	NA	NA

1,2-Dibromo-3-chloropropane	96-12-8	0.11	15	0.02	0.05	15
1.2-Dibromoethane/ Ethylene dibromide	106-93-4	0.028	15	0.02	0.05	15
Dibromomethane	74-95-3	0.11	15	0.01	0.05	15
m-Dichlorobenzene	541-73-1	0.036	6.0	0.33	0.67	6.0
o-Dichlorobenzene	95-50-1	0.088	6.0	0.33	0.67	6.0
p-Dichlorobenzene	106-46-7	0.090	6.0	0.33	0.67	6.0
Dichlorodifluoromethane	75-71-8	0.23	7.2	0.01	0.05	7.2
1, 1-Dichloroethane	75-34-3	0.059	6.0	0.005	0.005	6.0
1,2-Dichloroethane	107-06-2	0.21	6.0	0.005	0.005	6.0
1,1-Dichloroethylene	75-35-4	0.025	6.0	0.005	0.005	6.0
trans-1,2-Dichloroethylene	156-60-5	0.054	30	0.005	0.005	30
2,4-Dichlorophenol	120-83-2	0.044	14	0.33	0.67	14
2,6-Dichlorop henol	87-65-0	0.044	14	0.33	0.67	14
2,4-Dichlo phenoxyacetic acid/2,4-D	94-75-7	0.72	10	10	10	10
1,2-Dichloropropane	78-87-5	0.85	18	0.005	0.005	18
cis-1,3-Dichloropropylene	10061-01-5	0.036	18	0.005	0.005	18
trans-1,3-Dichloropropylene	10061-02-6	0.036	18	0.005	0.005	18
Dieldrin	60-57-1	0.017	0.13	0.01	0.01	0.13
Diethylene glycol, dicarbamate (6)	5952-26-1	.0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Diethyl phthalate	84-66-2	0.20	28	0.33	0.67	28
p-Dimethylamino-azobenzene	60-11-7	0.130	NA	0.33	NA	NA
2,4-Dimethyl phenol	105-67-9	0.036	14	0.33	0.67	14
Dimethyl phthalate	131-11-3	0.047	28	0.33	0.67	28
Dimetilan (6)	644-64-4	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Di-n-butyl phthalate	84-74-2	0.057	28	0.33	0.67	28
1,4-Dinitrobenzene	100-25-4	0.32	2.3	1.65	1.6	2.3
4,6-Dinitro-o-cresol	534-52-1	0.28	160	1.65	3.3	160
2,4-Dinitrophenol	51-28-5	0.12	160	1.65	3.3	160
2,4-Dinitrotoluene	121-14-2	0.32	140	0.33	0.67	140
2,6-Dinitrotoluene	606-20-2	0.55	28	0.33	0.67	28
Di-n-octyl phthalate	117-84-0	0.017	28	0 33	0.67	28
Di-n-propylnitrosamine	621-64-7	0.40	14	0.33	0.67	14
1,4-Dioxane	123-91-1	12.0	170	0.33	0.5	0.1
Diphenylamine (difficult to distinguish from diphenylnitrosamine)	122-39-4	0.92	13	0.33	13	13
Diphenylnitrosamine (difficult to distinguish from diphenylamine)	86-30-6	0.92	13	0.33 cannot be separated from Dipheylamine	13 reported as Dipheylamine	13 reported as Dipheylamine
1,2-Diphenylhydrazine	122-66-7	0.087	NA	0.33	NA for nonwastewater, reported as decomposition product azobenzene for wastewater	NA
Disulfoton	298-04-4	0.017	62	0.02	0.03	6.2
Dithiocarbamates (total) (6)	137-30-4	0.028	28	**undetermined**	**undetermined**	**undetermined**
Endosulfan I	959-98-8	0.023	0.066	0.005	0.066	0.066
Endosulfan II	33213-46-9	0.029	0.13	0.01	0.13	0.13
Endosulfan sulfate	1031-07-8	0.029	0.13	0.01	0.13	0.13
Endrin	72-20-8	0.0028	0.13	0.01	0.13	0.13
Endrin aldehyde	7421-93-4	0.025	0.13	0.01	0.13	0.13
EPTC (6)	759-94-4	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Ethyl acetate	141-78-6	0.34	33	0.01	33	33
Ethyl benzene	100-41-4	0.057	10	0.005	0.005	10
Ethyl cyanide/ Propanenitrile	107-12-0	0.24	360	0.25	360	360
Ethyl ether	60-29-7	0.12	160	0.01	160	160

bis(2-Ethylthexyl) phthalate	117-81-7	0.28	28	0.33	0.67	28
Ethyl methacrylate late	97-63-2	0.14	160	0.33	0.05	160
Ethylene oxide	75-21-8	0.12	NA	10	NA	NA
Famphur	52-85-7	0.017	15	0.1	1.3	15
Fluoranthene	206-44-0	0.068	3.4	0.33	0.67	3.4
Fluorene	86-73-7	0.059	3.4	0.33	0.67	3.4
Formetanate hydrochloride (6)	23422-53-9	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Formparanate (6)	17702-57-7	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Heptachlor	76-44-8	0.0012	0.066	0.005	0.002	0.066
Heptachlor epoxide	1024-57-3	0.016	0.066	0.005	0.056	0.066
Hexachlorobenzene	118-74-1	0.055	10	0.33	0.67	10
Hexachlorobutadiene	87-68-3	0.055	5.6	0.33	0.67	5.6
Hexachlorocyclo-pentadiene	77-47-4	0.057	2.4	0.33	0.67	2.4
HxCDDs (All Hexa-chlorodibenzo-p-dioxins)	NA	0.000063	0.001	0.0005	0.001	0.001
HxCDFs (All Hexa-chlorodibenzo-furans)	NA	0.000063	0.001	0.0005	0.001	0.001
Hexachloroethane	67-72-1	0.055	30	0.33	0.67	30
Hexachloropropylene	1888-71-7	0.035	30	0.33	0.67	30
Indeno (1,2,3-c,d) pyrene	193-39-5	0.0055	3.4	0.33	0.67	3.4
Iodomethane	74-88-4	0.19	65	0.01	0.05	65
Isobutyl alcohol	79-83-1	5.6	170	0.1	5	170
Isodrin	465-73-6	0.021	0.066	0.1	**0.66**	0.066
Isolan (6)	119-38-0	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Isosafrole	120-58-1	0.081	2.6	0.33	0.67	2.6
Kepone	143-50-0	0.001	0.13	0.05	**1.3**	0.13
Methacrylnitrile	126-98-7	0.24	84	0.02	0.05	84
Methanol	67-56 -1	5.6	0.75 mg/l TCLP	**5 mg/l TCLP**	Analyzed as total 10 mg/kg, equivalent to 0.5 mg/l TCLP	0.75 mg/l TCLP
Methapyrilene	91-80-5	0.081	1.5	0.33	0.67	1.5
Methiocarb (6)	2032-65-7	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Methomyl (6)	16752-77-5	0.028	0.14	**undetermined**	**undetermined**	**undetermined**
Methoxychlor	72-43-5	0.25	0.18	0.05	0.12	0.18
3-Methylcholanthrene	56-49-5	0.0055	15	0.33	0.67	15
4,4-Methylene bis(2-chloroaniline)	101-14-4	0.50	30	1.65	30	30
Methylene chloride	75-09-2	0.089	30	0.005	0.005	30
Methyl ethyl ketone	78-93-3	0.28	36	0.01	0.01	36
Methyl isobutyl ketone	108-10-1	0.14	33	0.01	0.01	33
Methyl methacrylate	80-62-6	0.14	160	0.33	0.05	160
Methyl methansulfonate	66-27-3	0.018	NA	0.33	NA	NA
Methyl parathion	298-00-4	0.014	4.6	0.02	0.06	4.6
Metolcarb (6)	1129-41-5	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Mexacarbate (6)	315-18-4	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Molinate (6)	2212-67-1	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Naphthalene	91-20-3	0.059	5.6	0.33	0.67	5.6
2-Naphthylamine	91-59-8	0.52	NA	0.33	NA	NA
o-Nitroaniline	88-74-4	0.27	14	1.65	3.3	14
p-Nitroaniline	100-01-6	0.028	28	1.65	3.3	28
Nitrobenzene	98-95-3	0.068	14	0.33	0.67	14
5-Nitro-o-toluidine	99-55-8	0.32	28	0.33	0.67	28
o-Nitrophenol	88-75-5	0.028	13	33	0.67	13
p-Nitrophenol	100-02-7	0.12	29	1.65	3.3	29
N-Nitrosodiethylamine	55-18-5	0.40	28	0.33	0.67	28
N-Nitrosodimethylamine	62-75-9	0.40	2.3	0.33	67	2.3
N-Nitroso-di-n-butylamine	924-16-3	0.40	17	0.33	0.67	17
N-Nitrosomorpholine	59-89-2	0.40	2.3	0.33	0.67	2.3
N-Nitrosopiperidine	100-75-4	0.013	35	1.65	1.3	**undetermined**
N-Nitrosomethyl-ethylamine	10595-95-6	0.40	2.3	0.33	0.67	2.3
N-Nitrosopyrrolidine	930-55-2	0.013	35	0.33	0.67	**undetermined**

Oxamyl (6)	23135-22-0	0.056	0.28	**undetermined**	**undetermined**	**undetermined**
Parathion	56-38-2	0.014	4.6	0.02	0.03	4.6
Total PCBs (sum of all PCB isomers, or all Aroclors)	1336-36-3	0.10	10	0.8	10	10
Pebulate (6)	1114-71-2	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Pentachlorobenzene	608-93-5	0.055	10	0.33	0.67	10
PeCDDs (All Pentachlorodibenzo-p-dioxins)	NA	0.000063	0.001	0.0005	0.001	0.001
PeCDFS (All Penta-hlorodibenzo-furans)	NA	0.000035	0.001	0.0005	0.001	0.001
Pentachloroethane	76-01-7	0.055	6.0	0.33	0.01	6.0
Pentachloronitrobenzene	82-68-8	0.055	4.8	1.65	0.67	4.8
Pentachlorophenol	87-86-5	0.089	7.4	1.65	3.3	7.4
Phenacetin	62-44-2	0.081	16	0.33	0.67	16
Phenanthrene	85-01-9	0.059	5.6	0.33	0.67	5.6
Phenol	108-95-2	0.039	6.2	0.33	0.67	6.2
o-Phenylenediamine (6)	95-54-5	0.056	5.6	**undetermined**	**undetermined**	**undetermined**
Phorate	298-02-2	0.021	4.6	0.02	0.02	4.6
Phthalic acid	100-21-0	0.055	28	3.3	28 reported as Phthalic anhydride	**undetermined**
Phthalic anhydride	85-44-9	0.055	28	0.66	28	**undetermined**
Physostigmine (6)	57-47-6	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Physostigmine salicylate (6)	57-64-7	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Promecarb (6)	2631-37-0	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Pronamide	23950-58-5	0.093	1.5	0.33	0.67	1.5
Propham (6)	122-42-9	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Propoxur (6)	114-26-1	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Prosulfocarb (6)	52888-80-9	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Pyrene	129-00-0	0.067	8.2	0.33	0.67	8.2
Pyridine	110-86-1	0.014	16	0.33	0.67	16
Safrole	94-59-7	0.081	22	0.33	0.67	22
Silvex/2,4,5-TP	93-72-1	0.72	7.9	7.9	7.9	7.9
1,2,4,5-Tetrachloro-benzene	95-94-3	0.055	14	0.33	0.67	14
TCDDs (All Tetrachlorodi-benzo-p-dioxins)	NA	0.000063	0.001	0.0005	0.001	0.001
TCDFS (All Tetra-chlorodibenzofurans)	NA	0.000063	0.001	0.0005	0.001	0.001
1,1,1,2-Tetrachloroethane	630-20-6	0.057	6.0	0.01	0.05	6.0
1,1,2,2-Tetrachloroethane	79-34-5 1	0.057	6.0	0.005	0.005	6.0
Tetrachloroethylene	127-18-4	0.056	6.0	0.005	0.005	6.0
2,3,4,6-Tetrachlorophenol	58-90-2	0.030	7.4	0.33	0.67	7.4
Thiodicarb (6)	59669-26-0	0.019	1.4	**undetermined**	**undetermined**	**undetermined**
Thiophanate-methyl (6)	23564-05-8	0.056	1.4	**undetermined**	**undetermined**	**undetermined**
Tirpate (6)	26419-73-8	0.056	0.28	**undetermined**	**undetermined**	**undetermined**
Toluene	108-88-3	0.080	10	0.005	0.005	10
Toxaphene	8001-35-2	0.0095	2.6	0.5	0.16	2.6
Triallate (6)	2303-17-5	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Tribromomethane/ Bromoform	75-25-2	0.63	15	0.005	0.005	15
1,2,4-Trichlorobenzene	120-82-1	0.055	19	0.33	0.67	19
1,1,1-Trichloroethane	71-55-6	0.054	6.0	0.005	0.005	6.0
1,1,2-Trichloroethane	79-00-5	0.054	6.0	0.005	0.005	6.0
Trichloroethylene	79-01-6	0.054	6.0	0.005	0.005	6.0
Trichloromonofluoro-methane	75-69-4	0.020	30	0.005	0.005	30
2,4,5-Trichlorophenol)	95-95-4	0.18	7.4	1.65	3.3	7.4
2,4,6-Trichlorophenol	88-06-2	0.035	7.4	0.33	0.67	7.4
2,4,5-Trichlorophen-oxyacetic acid/2,4,5-T	93-76-5	0.72	7.9	7.9	7.9	7.9
1,2,3-Trichloropropane	96-18-1	0.85	30	0.01	0.05	30

1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	0.057	30	0.01	0.05	30
Triethylamine (6)	10-144-8	0.081	1.5	**undetermined**	**undetermined**	**undetermined**
tris-(2,3-Dibromopropyl) phosphate	126-72-7	0.11	0.10	**3.3**	**0.33**	**undetermined**
Vernolate (6)	1929-77-7	0.042	1.4	**undetermined**	**undetermined**	**undetermined**
Vinyl chloride	75-01-4	0.27	6.0	0.01	0.05	6.0
Xylenes-mixed isomers (sum of o-, on, and p-xylene	133020-7	0.32	30	0.005	0.005	30

Footnotes to Universal Treatment Standards Table:

(1) CAS means Chemical Abstract Services. When the waste code and/or regulated constituents we described as a combination of a chemical with it's salts and/or esters; the CAS number is given for the parent compound only.

(2) Concentration standards for wastewaters are expressed in mg/l and are based on analysis of composite samples.

(3) Except for Metals (EP or TCLP) and Cyanides (Total and Amemable) the nonwastewater treatment standards expressed as a concentration were established, in part, based upon incineration in units operated in accordance with the technical requirements of 40 CFR part 264, subpart O, or 40 CFR part 265, subpart O, or based upon combustion in fuel substitution units operating in accordance with applicable technical requirements. A facility may comply with these treatment standards according to provisions in See 268.40(d). All concentration standards for nonwastewaters are based on analysis of grab samples.

(4) Both Cyanides (Total) and Cyanides (Amenable) for nonwastewaters are to be antlyzed using Method 9010 or 9012, found in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods". EPA Publication SW-846, as incorporated by reference in 40 CFR 260.11, with a sample size of 10 grams and a distillation time of one hour and 15 minutes.

(5) These constituents am not "underlying hazardous constituents" in characteristic news, according to the definition at See. 268.2(i).

(6) Between August 26, 1997, and August 26, 1998, these constituents are not "underlying hazardous constituents" as defined at Sec. 268.2(i).

REFERENCES

Protection of the Environment, 40 Code of Federal Regulations.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW-846 Third Edition, United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C., December, 1996.

RCRA Regulations and Keyword Index, Elsevier Science Inc., New York, New York, 1997 Edition.

IGNITABILITY PERFORMANCE EVALUATION STUDY ARE YOUR WASTE STREAMS BEING CORRECTLY CHARACTERIZED?

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ABSTRACT

Thirteen commercial laboratories were evaluated for consideration of providing waste stream characterization support. An initial single-blind performance evaluation (PE) study was performed to determine the accuracy of the laboratory-reported results when compared to known values.

The initial PE study was conducted for constituents typically analyzed for hazardous waste characterization. These constituents included Toxicity Characteristic Leaching Procedure (TCLP) volatiles, TCLP semivolatiles, TCLP metals, and ignitability. A review of the ignitability tests performed by SW-846 Method 1010 and 1020 exhibited a wide range of both positive and negative bias from the known flashpoint temperature of the pure compound used as the PE sample. Results were compared to reproducibility criteria generated from American Society of Testing Materials (ASTM) Method D93-96.

Because of the erratic ignitability results observed for many of the participating laboratories, the laboratories were requested to perform a self-audit inspection of their current SOP and actual laboratory procedures. These self-audit results were used to ensure inter-laboratory consistency and compliance to SW-846 Method 1010 and Method 1020.

A second round of PE samples were subsequently submitted to each of the thirteen participating laboratories for analysis. These results showed some improvement for several of the laboratories, whereas other laboratories again reported results with a significant bias. The results of this study exhibited a wide range of ignitabilities which would have represented incorrect waste characterization if the PE samples were actual waste stream samples. This paper will focus on discussion of the PE sample results, the laboratory self-audit results, and method compliance issues.

INTRODUCTION

A comprehensive laboratory evaluation process was performed to identify commercial laboratories to provide waste characterization testing services. This evaluation included an initial technical survey of approximately 40 laboratories. The survey results were used to further reduce the potential candidates to 13 laboratories. Laboratory audits specifically focused on waste characterization analyses and performance evaluation (PE) samples for specific parameters of interest for the characterization of complex wastes was used to further evaluate the 13 short-listed laboratories. The parameters included ignitability, TCLP volatiles, TCLP semivolatiles, and TCLP metals. An initial set of single-blind PE samples were prepared as whole volume samples by a reputable commercial PE provider.

A single-blind PE study sample is defined as a "test" sample in which the laboratory is aware that the sample submitted is a PE sample but does not have knowledge relative to the analytes or true concentrations contained in the PE. A single-blind sample permits the data user to better understand a laboratory's analytical accuracy and by inference, draw conclusions on the accuracy of actual waste sample results.

The matrix of the ignitability PE sample was a pure compound. The TCLP volatile sample was an aqueous matrix, and the TCLP metals sample was a soil matrix. The PE samples for all 13 laboratories were prepared from the same lot number to further reduce variance and permit a direct and meaningful comparison between laboratories. Whole-volume samples, which require no further dilution or preparation by the laboratory prior to analysis, were chosen to further reduce variables caused by different technicians or chemists. The PE samples were prepared and shipped on ice under Chain-of-Custody procedures to each laboratory directly from the provider.

In addition, an actual complex industrial waste stream sample was also used in this PE study. This waste stream was selected to provide the laboratories with a representative "real-world" sample that the laboratories may receive as an actual sample for waste testing. In particular, a paint purge solvent was selected for testing. This paint purge solvent is relatively homogeneous and has previously been characterized as hazardous due to a flashpoint temperature below the regulatory limit and volatile concentrations above the regulatory limit.

To collect this sample, the PE provider furnished bottles to the industrial facility for packaging this solvent. This sample was collected and shipped back to the PE provider for homogenization and repackaging for delivery to the 13 laboratories. This PE sample was shipped by ground carrier and was not refrigerated. Since it was not certified, this sample was to be evaluated only for interlaboratory comparison purposes and was analyzed for ignitability, TCLP volatiles and TCLP metals.

Performance by the individual laboratories was evaluated not only for the results proximity to the certified values but also for communications, data packaging and reporting, method compliance, and timeliness of deliverables. These latter issues were evaluated using techniques and procedures addressed in a previous manuscript (Dupes and Rose, 1995). The issues are not discussed any further herein.

INITIAL PERFORMANCE EVALUATION SAMPLE RESULTS

In general, the laboratories reported acceptable results for the TCLP volatile organic compounds and metals, relative to the program requirements. However, ignitability results ranged from 114ºF to 153ºF, with only four laboratories meeting acceptance criteria for this parameter. The ignitability PE sample was certified by the provider of the pure compound to have a flashpoint of 140ºF ± 5ºF. This certified value represents the flashpoint of the compound as determined by various manufacturers of this compound. The temperature of the PE sample was specifically chosen to determine variance around 140ºF. This temperature is also defined as the regulatory limit for characterization of the waste as hazardous. Wastes that flash at a temperature of <140ºF are considered hazardous and wastes that flash at >140ºF are considered non-hazardous by the definition for ignitability (40 CFR Part 261).

Ten of the laboratories reported the temperatures higher than the regulatory limit of 140ºF. resulting in a classification as non-hazardous. Results for the three laboratories classifying the PE sample as hazardous reported results of 129ºF, 114ºF, and 120ºF. Those temperatures are all well below the lower acceptance limits of 135ºF for the PE sample. Six other laboratories were slightly above the 145ºF acceptance criteria. A summary of the results is presented in Table 1.

The "real world" purge solvent sample submitted to the laboratories was consistently identified by all laboratories as hazardous based on flashpoint. The reported flashpoints ranged from 66-76ºF (several laboratories reported the sample flashed at less than their reporting limit of room temperature).

The variance in the certified (pure compound) PE results may have been due to the use of thermometers which have not been adequately calibrated against a National Institute of Standards and Technology (NIST) standard thermometer (this is routinely noted in a number of audits recently performed by the authors), the lack of correction for barometric pressure, or analytical variance of the methodologies used by the laboratories. Each of the laboratories management or quality assurance staff were required to conduct an intensive self-audit review of the PE sample analysis, general analysis conditions, and quality control procedures to determine potential causes for the wide range of flashpoint temperatures obtained for the PE sample.

SELF-AUDIT QUESTIONS AND FINDINGS

Upon completion of the initial PE study, a self-audit questionnaire was generated for completion by each of the participating laboratories. The audit questionnaire consisted of 26 questions obtained from a technical review of SW-846 Methods 1010 and 1020A; ASTM Methods D93-80, D93-90, D93-96, D3278-96, and E502-84. These questions included verification of the method used and referenced for analysis of the initial PE study sample, sample storage conditions, instrument analysis conditions, analysis procedures, thermometer calibrations, quality control measures, acceptance criteria, and corrective actions.

The questionnaire was provided to each of the laboratories for completion by laboratory management or quality assurance personnel. In addition to providing written responses to the questions, a copy of the laboratory standard operating procedure was requested for review.

A review of the thirteen laboratory responses and SOPs were conducted to determine possible reasons for the significant variation observed. A summary of issues identified in the self-audit checklists by the authors is presented below.

- According to the original request for analysis, all laboratories were requested to perform Method 1020A. Several laboratories did request a change to Method 1010, which was granted and documented. However, many laboratories did not request this change. Whenever a method change is necessary, data users (viz., the client) should be contacted prior to implementing the method change.

- Several laboratories used compounds (i.e. acetic acid, mixed xylene, and kerosene) that were not stated in the method for quality control purposes. The laboratories were directed to use *p*-xylene conforming to the ASTM specifications, as required by Method 1010. The acceptance criteria should be 81±2ºF as required by ASTM D93-90 or 81±1ºF as required by ASTM D93-96.

- Several laboratories did not store the ignitability PE sample at 4±2ºC. Although it could be argued that a pure single-component compound used for the PE would be unaffected by volatile constituent loss, actual waste samples are typically complex mixtures, and lighter fractions can be lost due to volatilization. All laboratories were requested to store future samples scheduled for ignitability at 4±2ºC to reduce the possibility of loss of lighter fraction volatile constituents.

- Five laboratories had not calibrated or could not demonstrate that the thermometer used for ignitability determination had been calibrated with a NIST-standard thermometer within the last year. One laboratory noted a 2-5ºF difference upon calibration of three different thermometers. In addition, a laboratory also noted that after the recalibration a mercury gap in one thermometer was noted and that the gap increased as the temperature increased. All laboratories were directed to recalibrate the thermometers on an annual basis. A multi-point calibration should be performed to determine accuracy at several temperatures, and correction factors must be taken into account when measuring flashpoint temperatures.

- Six laboratories did not correct for barometric pressure, as required by the ASTM D93 methods. Several of the laboratories noted that the correction would be very small (< 0.2ºF); however, one laboratory noted the flashpoint temperature would increase by 0.9ºF. All laboratories were directed to correct for the ambient barometric pressure of the laboratory, as required by ASTM methodologies referenced in Method 1010 and Method 1020A.

- Many of the laboratories did not report a duplicate result for the ignitability analysis by Method 1010. Although not specifically stated in Method 1010 or ASTM D93, duplicate analyses of all samples should be performed to comply with ASTM E502, which indicates that the average results for flashpoint should be reported. This will also provide a consistent approach with respect to Method 1020A, which requires duplicate analyses. Sufficient volume (>150 ml) should be collected or provided in order to conduct duplicate analyses by Method 1010.

- All laboratories indicated the Pensky Martens apparatus used for analysis by Method 1010 is located in a hood to reduce surrounding drafts and for health and safety considerations. However, several laboratories indicated that the hood was turned on during the actual testing, which can cause loss of volatiles through drafts. Several laboratories indicated that problems have occurred when hoods containing the apparatus are turned on during analysis. Laboratories were directed to limit the amount of draft around the apparatus.

- Three laboratories did not meet *p*-xylene acceptance criteria of 81±2ºF (ASTM D9390) or 81±1ºF (ASTM D93-96) prior to analysis of the PE sample. One laboratory reported an acceptance range for *p*-xylene of 80-91ºF. Two laboratories did not report *p*-xylene results on the logbook pages. These practices are not acceptable. All *p*-xylene calibrations must meet acceptance criteria and be recorded prior to sample analysis. Several laboratories have implemented the use of an additional laboratory control sample (LCS) near the regulatory limit of 140ºF. This is not a method requirement but is recognized as a good laboratory practice.

- One laboratory was increasing the rate of temperature of the sample by 2ºF/minute ; prior to application of the test flame. The laboratories were directed to follow the rate of temperature increase, as specified in the ASTM D93 Method as 9-11ºF/minute.

- One laboratory reported that the sample was stirred during the actual application of the test flame to the sample. Samples must not be stirred during the application of, the test flame to the vapor space, as required by the ASTM method.

- Several laboratories indicated the introduction of the test flame into the vapor space is maintained from 0.5-1.5 seconds. Analysts should attempt to consistently introduce the test flame into the vapor space for 1 second, as required by the ASTM protocol referenced by Method 1010.

- One laboratory reported the ignitability results to the nearest tenth degree. One laboratory reported the raw results on a stenopad, which did not include, the analysis test name, method number, analyst name, laboratory name, or QC results. The laboratories were directed to report result to the nearest 1ºF. Adequate documentation of quality control (QC) results, barometric pressure, analysis date, etc. must be maintained by all laboratories through the use of formal logbooks.

- Several laboratories had not reviewed their SOP within the last year to verify method compliance and actual laboratory procedures. All laboratories were directed to review and update laboratory SOPs on an annual basis to reflect the actual procedures performed and to monitor for continuing method compliance.

SECOND ROUND IGNITABILITY PE STUDY

Upon completion of the self-audit review, laboratories were notified of the findings and requested corrective actions prior to performing the second ignitability PE sample study. Three ignitability PE samples were selected for the second round study. The flashpoint of the PE samples was specifically designed by the authors to provide a range of flashpoints. The flashpoint-certified values of Flashpoint Sample #1, Flashpoint Sample #2, and Flashpoint Sample #3 were 140ºF, 120ºF, and 170ºF, respectively. These three flashpoints provide a sample that would be considered hazardous (120ºF), a sample at the hazardous regulatory limit (140ºF) and a sample that would be considered non-hazardous (170ºF). The actual compounds used for the PE samples were chosen and prepared by the same commercial PE provider used for the initial study. The expected flashpoint temperature represents the flashpoint for the compound as determined by various manufacturers of this compound. All PE samples were pretested prior to use by the PE supplier by Pensky Martens closed-cup procedures (US EPA SW-846 Method 1010) and were corrected for barometric pressure of 620 mm. All PE samples were contained in glass bottles with Teflon-lined caps and were shipped on ice under Chain-of-Custody to the 13 participating analytical laboratories. Sufficient volume (150 ml) was sent to each laboratory to permit duplicate analyses of the PE sample.

ANALYTICAL RESULTS AND CRITERIA FOR EVALUATION

Reproducibility criteria were calculated based on ASTM D93-96, which provides precision and bias data for the ASTM method. Reproducibility in this ASTM method is defined as "the difference between two single and independent results obtained by different operators working in different laboratories on identical material that would, in the long run, in the normal and correct operation of the test method, exceed the following values only one case in 20" (ASTM D93-96).

where:

$R=BX$

$B = 0.078$
X = the reported result in °C
R = reproducibility

Since the ASTM method is unclear as to which temperature should be used in calculating the reproducibility criteria, criteria for the three flashpoint PE samples were generated by using the expected flashpoint (converted to degrees Celsius) in the equation listed above. The criteria calculated should represent a range encompassing the expected value of the PE sample. The following criteria were calculated for the PE samples:

Sample Identifier	Expected Flashpoint	Reproducibilily Criteria
Flashpoint Sample #1	140°F	± 8°F
Flashpoint Sample #2	120°F	± 7°F
Flashpoint Sample #3	170°F	± 11°F

According to the previous ASTM Method revision D93-90, reproducibility criterion of ± 6°F should be used for evaluation of the analytical data. According to the ASTM D93-90 method, this criteria applies to all liquid samples with flashpoint temperatures less than 220°F. Evaluation of the data using the more stringent criteria in D93-90 excluded only two more results when compared to the criteria calculated by Method D93-96. A summary of the results are presented in Tables 2, 3 and 4.

All participating laboratories except one analyzed the three PE samples by SW-846 Method 1010. One laboratory analyzed the samples by SW-846 Method 1020. Three provided results after the due date, missing the specifically stated date as a requirement in the documentation accompanying the PE samples.

DISCUSSION OF SECOND ROUND IGNITABILITY PE STUDY RESULTS

Upon review of the PE sample results, the inter-laboratory accuracy of the results obtained from the laboratories was observed to be variable. Four laboratories reported results which, when compared to the known flashpoint, were greater than the Method D93-96 criteria for all analyses (except for the analysis of Flashpoint #1 sample by one laboratory, which was within criteria). Reported results, when compared to the known flashpoint, ranged from 10° to 70°F absolute difference from the known value of the PE samples. Results reported by one laboratory were biased very low (-27° to -70°F below the known flashpoints of the materials). Results reported by the laboratories are unacceptable and may indicate a recurring problem relating to the analyses being performed by these laboratories.

Two laboratories reported two of the three results outside the Method D93-96 criteria. When compared to the known flashpoint, reported results ranged from 8° to 12°F absolute difference from the known value of the PE samples.

Five laboratories reported one of the three results outside the calculated Method D93-96 criteria. When compared to the known flashpoint, reported results ranged from 7° to 13°F absolute difference from the known value of the PE samples. One laboratory reported duplicate results, but did not report and average result for each PE sample. Finally, two laboratories reported results for all three of the PE samples within the Method D93-96 criteria.

In general, a majority of the laboratories reported a positive bias when compared to the known flashpoints of the samples. Furthermore, several laboratories did not follow the instructions provided after the self-audit. Two laboratories did not report the results to the nearest 1ºF. Instead, the laboratories reported results to one decimal place. In addition, two laboratories did not analyze all samples in duplicate as requested. Finally, one laboratory sent the PE samples from the facility being considered for program inclusion, where ignitability is apparently no longer performed, to an affiliated network laboratory. This transfer occurred without notification to the authors. This network facility was not previously audited for this program.

SUMMARY

Based upon a review of the initial ignitability study, self-audit review, and subsequent PE study, the use of ignitability data for actual waste testing should be highly scrutinized. The regulatory-approved methods require a significant amount of operator experience in conducting tests that are consistent and method compliant. Evaluating ignitability through audits and frequent double-blind PE studies should be implemented to verify acceptable performance. Without continuous review of this method, inaccurate ignitability results could be causing your waste to be disposed of improperly.

ACKNOWLEDGMENTS

Mr. Chuck Wibby and Environmental Resource Associates for providing technical assistance in identification and evaluation of compounds for the ignitability performance evaluation study, providing assistance in collection, homogenization, and repackaging of the Chrysler waste stream sample and supply of all PE samples in this study.

Mr. Brian Miller, of Chrysler Corporation for collection, packaging, and shipment of the waste stream sample used in this PE study.

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Table 1. Initial Ignitability Performance Evaluation Study

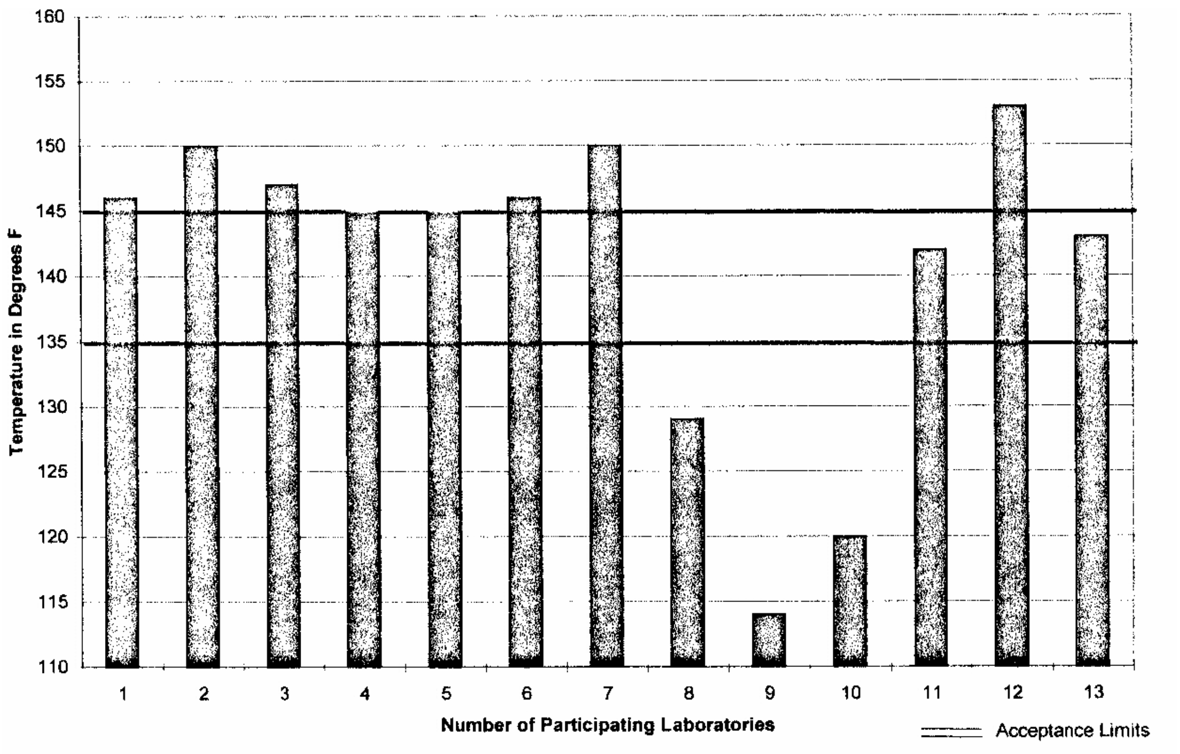


Table 2. Ignitability Performance Evaluation Study PE Flashpoint Sample #1

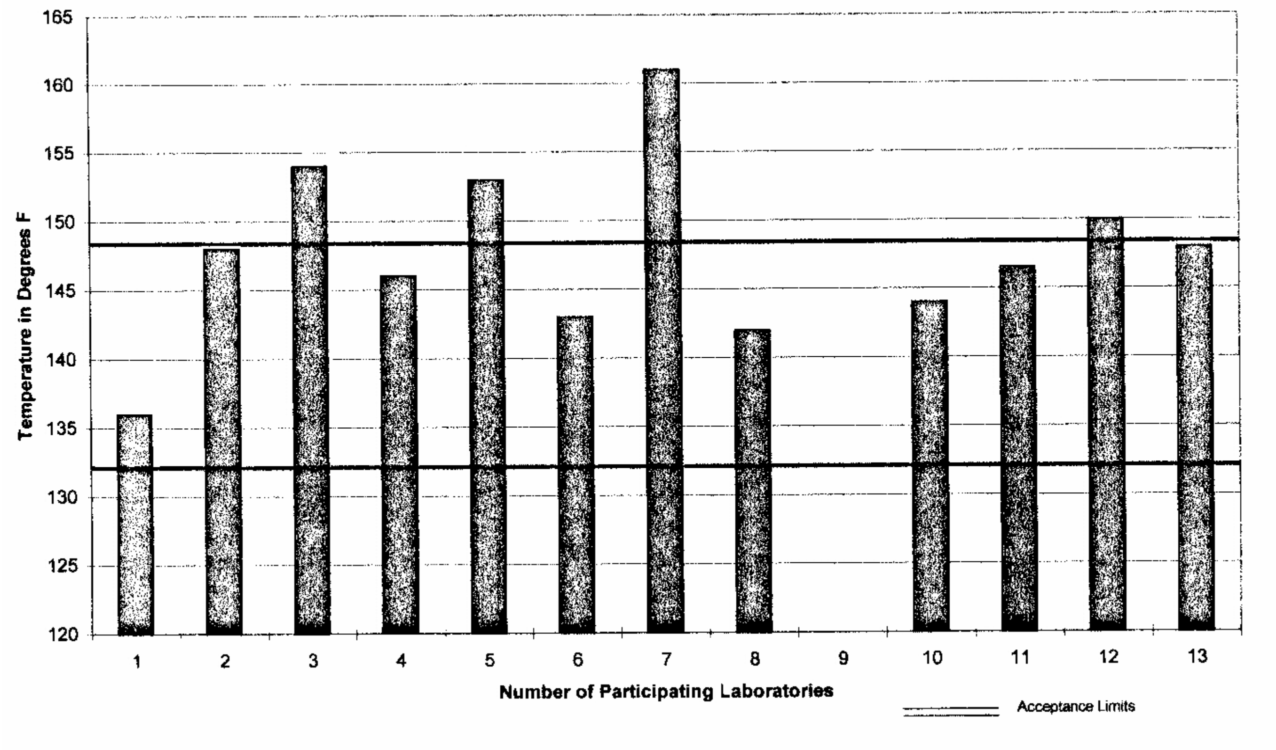


Table 3. Ignitability Performance Evaluation Study PE Flashpoint Sample #2

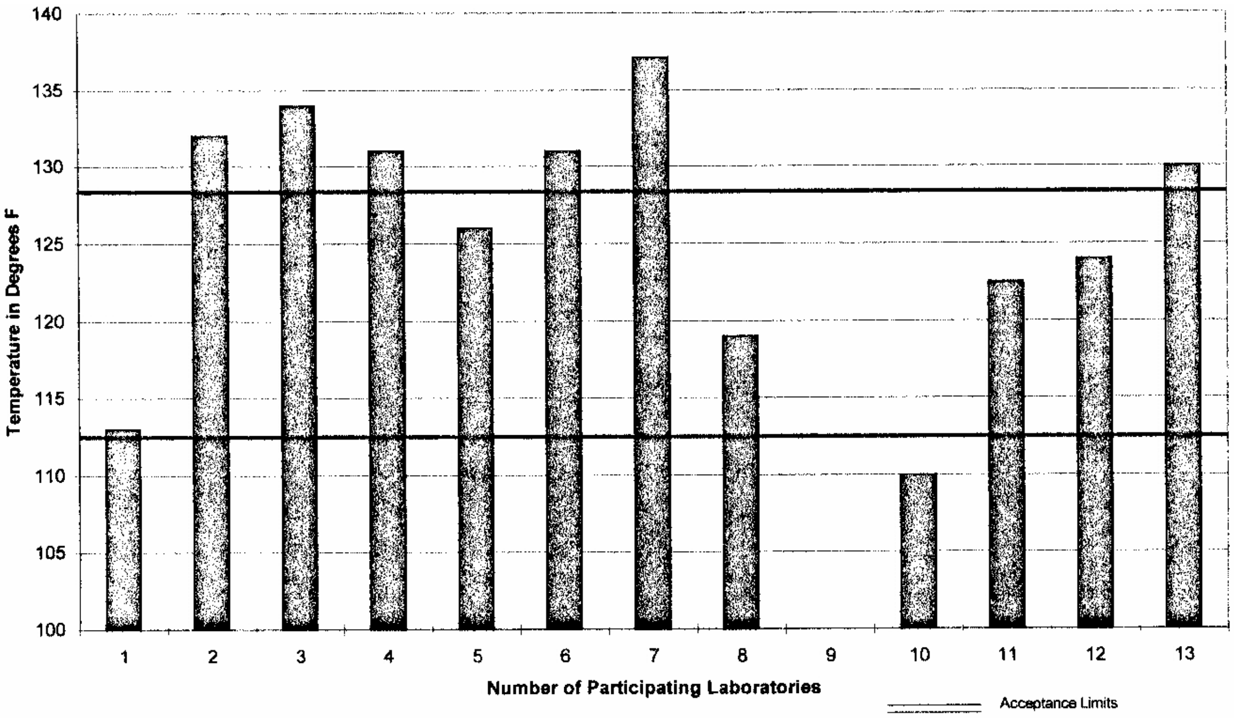
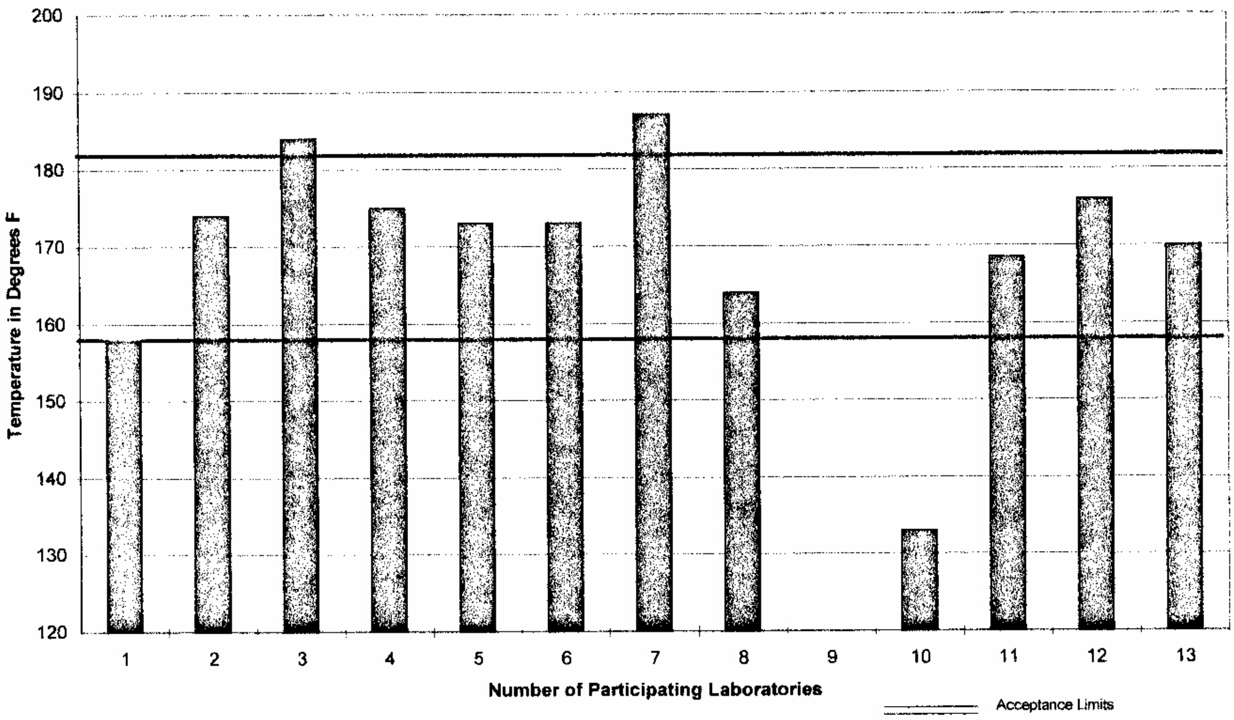


Table 4. Ignitability Performance Evaluation Study PE Flashpoint Sample #3



TECHNIQUES FOR IMPROVING THE ACCURACY OF CALIBRATION IN THE ENVIRONMENTAL LABORATORY

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Abstract

Consistent and reliable procedures for generating calibrations are essential to accurate laboratory results. Unfortunately the interpretation of acceptable practice is often based on misunderstanding or derived from practices commonly utilized in non-environmental methods, and therefore does not provide a reliable means for maintaining data quality. This paper presents a demonstration that some common practices used in the calculation and evaluation of calibration factors, including the use of unweighted regression and the associated correlation coefficient, are inappropriate for environmental analysis due to high relative errors which result at the low end of the curve. Alternate criteria for evaluation of calibration curves are proposed based on the Relative Standard Error (%RSE). Statistical derivations and examples are presented to demonstrate how this approach provides an improved measure for the evaluation of calibration data based on weighted regression. Other related considerations for assessing acceptability of calibration data are also presented.

Introduction

Any analytical measurement must employ reference elements to ensure traceability to relevant basic quantities. The quality of a calibration depends on the uncertainty of the reference, the appropriateness of the reference and how well the calculation procedures match the requirements of the analysis. A majority of the methods employed in the environmental laboratory are based on a relative calibration where standards of known content and concentration are analyzed by a suitable detector. The responses of samples analyzed under the same conditions are then used to calculate concentrations by numerical interpolation to a response curve from the calibration standards.

The only criterion for initial calibration in SW-846 method 8000A[1] reads, *"If %RSD is less than 20 an average calibration factor can be used otherwise data should be fitted to a curve."* There are many examples of well defined and reproducible calibrations which either due to nonlinearity, or a non-zero intersection of the axis will not meet this 20% criterion for acceptability. Recognizing this, update III to SW-846, Method 8000B[2] provides additional direction on use mid evaluation of least squares regression, adding criteria for higher order curves. However, several critical issues are not sufficiently considered and overall the current guidance remains incomplete with regard to error weighitng and evaluation of acceptability.

Linear Calibration

The most commonly adopted option for handling calibration data, which is linear but does not meet the criteria for averaging, involves the calculation of coefficients for a linear equation of the form:

$$y = Ax + B \qquad \text{Equation 1}$$

Concentration is defined here as the independent variable (x) and response as the dependent variable (y) in compliance with method 8000B. A least squares regression is employed and the value of the correlation coefficient (r) or the coefficient of determination (r^2) is evaluated as a measure of acceptability. A value of 1.00 represents a perfect correlation. Generally in practice, a value of r^2 greater than 0.990 is considered satisfactory.

The practical difficulty encountered in this approach is displayed in Figure 1. For the example data set, the line based on an average calculation (shown as a dotted line) easily meets the 20% acceptance criteria for %RSD, yet r^2, does not meet the criteria for acceptability with a value of 0.928.

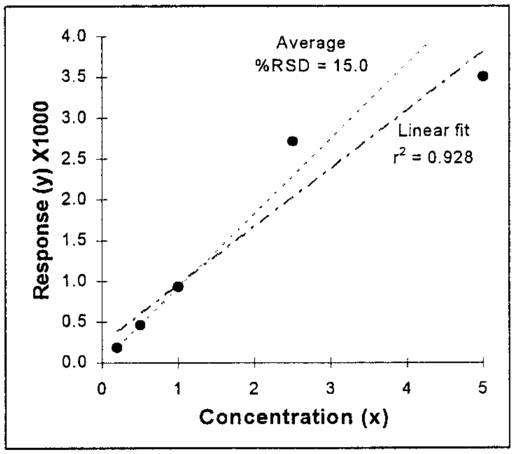


Figure 1

To understand this inconsistancy we must examine more closely the statistical difference between an average calculation and the regression line. The average calibration factor is determined according to equation 2.

$$\overline{C} = \frac{1}{n}\sum_{i=1}^{n} C_i \qquad \text{Equation 2}$$

Where:

$\overline{C}$ = Average Calibration factor
C_i = Calibration factor for calibration level i (y_i/x_i)
n = number *of* calibration levels

This and all following equations may also be adapted to internal standard methods by substituting the relative response calculated as in Equation 3 for the measured response (y_i).

$$y_i^{\text{Relative}} = y_i \, x \, \frac{x_i^{IS}}{y_i^{IS}} \qquad \text{Equation 3}$$

y_i = response of target analyte
x_i^{IS} = concentration of internal standard
y_i^{IS} = response of internal standard

Graphically the average and associated error limits based on ±1 standard deviation are shown in Figure 2. This type of normalized plot makes visual examination of the data more straight-forward[3] as values at the low end of the calibration are shown at the same relative scaling as those toward the high end.

The average represents the value which will minimize the variance in the calibration factors ($s^2{}_C$) for all calibration points[4]. For reference the calculation of variance is shown in Equation 4.

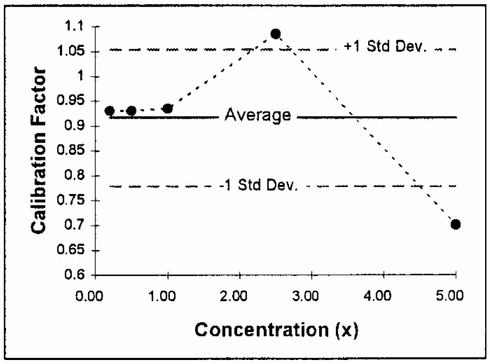


Figure 2

$$s_C^2 = \frac{\sum_{i=1}^{n}\left(C_i - \overline{C}\right)^2}{n-1} \qquad \text{Equation 4}$$

If $\hat{y}_i$ is defined as the expected response for calibration level i from the relationship $\hat{y}_i = x_i\overline{C}$, by substitution the variance can also be expressed as:

$$s_C^2 = \frac{\sum\left[\frac{y_i - \hat{y}}{x_i}\right]^2}{n-1} \qquad \text{Equation 5}$$

Using the method of least squares we can determine a mathematical relationship between the dependent and independent variables which minimizes the residual variance. By definition the residual variance represents the variability due to experimental error[5] and does not include that contribution to variance which is attributable to differences in the independent variable. The residual variance of y on x is defined as:

$$s_{yx}^2 = \frac{\sum_{i=1}^{n}(y_i - \hat{y})^2}{n-1} \qquad \text{Equation 6}$$

A comparison of equations 5 and 6 demonstrates that the average value is the same as a coefficient derived from least squares regression if a weighting of $1/x^2$ is applied. The average calibration factor gives a result which is identical to that produced by the method of least squares using (1/concentration^2) weighting and intercept forced through zero.

Alternatively a generalized equation for calculating the coefficient which fits the simple relationship $y = Ax$ and minimizes the residual variance without weighting is determined by substituting Ax for y in Equation 6 and setting the derivative with respect to A equal to zero. This gives for the calibration factor:

$$A = \frac{\sum_{i=1}^{n} x_i y_i}{\sum_{i=1}^{n} x_i^2} \qquad \text{Equation 7}$$

For the example data set, calibration coefficients and residual variances are compared in table 1. The coefficients determined from these two approaches are quite different and it is obvious that an average calibration coefficient does not minimize the residual variance of y on x.

Table 1

Calculation type	CF	s^2
Average	0.916	1.335
Linear fit	0.784	0.768

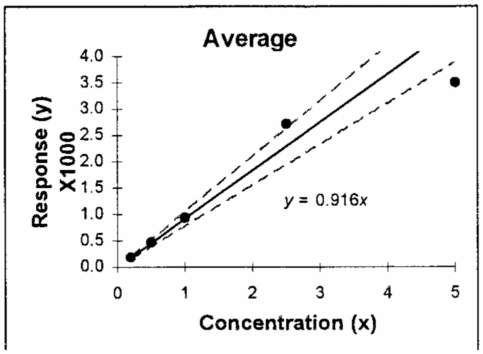


Figure 3

Transforming the vertical axis of Figure 2 to a non-normalized form gives the plot shown in Figure 3. A comparable plot for the unweighted regression line using the same set of example data is presented in Figure 4. Both figures represent graphically, with the dashed lines, effective error weighting based on ±1 standard deviation.

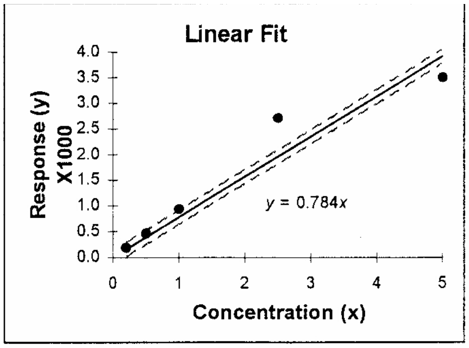


Figure 4

Figure 3 demonstrates that $1/x^2$ weighting gives a relationship that emphasizes precision at the low end of the calibration range. In environmental analyses frequently the objective is to ensure that target analytes do not exceed defined regulatory or action limits, hence reducing quantitation error at low concentrations is especially important.

Deriving the best form for a calibration curve must include consideration of the weighting factors which are appropriate to the requirements of the analysis. As was shown empirically for the single factor calibrations and can be proven for the general case[6], the value of the coefficients is sensitive to the weighting. Method 8000B requires that at least three replicates at a minimum of 5 concentration levels are used to derive weighting factors which are defined as the inverse of the standard deviation squared for each concentration. In practice this is an especially burdensome requirement, both in the amount of data required and the computational difficulty which results when using individually derived weighting values for each calibration level. Faced with the options in method 8000B, most laboratories will probably choose curve fitting without any consideration of weighting regardless of the potential negative impact on data quality.

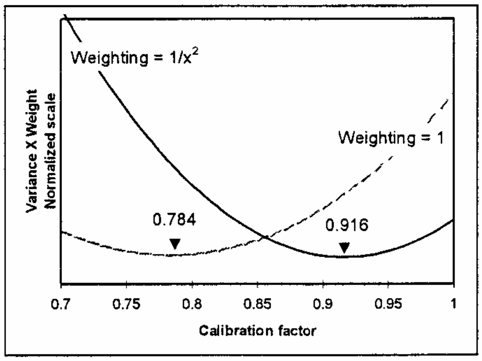
For many methods in the environmental laboratory errors in measurement are proportional to the magnitude of the parameter measured. Likewise it is common to consider percentage errors relative to the concentration as we have demonstrated in the case of the average calibration calculations. Rather than perform multiple replicates each time a calibration is run, the laboratory should make an initial determination of the relationship between concentration and the standard deviation throughout the calibration range, Where a direct proportionality is found, all subsequent calibrations should be based on the 1/concentration^2 weighting which is consistent with average calibration curves. Conversely, if standard deviations are of equal absolute magnitude throughout the concentration range, calibrations should be unweighted and average calibration factors should not be used. When the weighting is expressed as a function of the concentration most data systems are capable of perforating the calculation.

Percent Relative Standard Error

The magnitude of the residual variance with error weighting applied will provide a measure of the experimental error for the derived curve. Figure 5 shows the relationship between variance and calibration coefficient for a fitting equation of the form: $y = Ax$.

The value of relative standard deviation defined according to Equation 8 has widespread acceptance as a measure of the error associated with an average calibration.

$$\%RSD = 100x\frac{1}{\bar{C}}x\sqrt{\frac{\sum_{i=1}^{n}(\bar{C}\ \ C_i)^2}{n\ \ 1}} \qquad \text{Equation 8}$$



Because standard deviation is equal to the square root of variance, it can be shown that %RSD is also equal to the square root of the weighted residual variance of *y* on *x*, calculated as a percentage, using a derivation similar to that for Equation 5.

Likewise the coefficient of determination *(r^2)* is normally, recognized as an indication of error associated with regression curves.

Figure 5

$$r^2 = \frac{\sum(y\ \ \bar{y})^2\ \sum(y\ \ \hat{y})^2}{\sum(y\ \ \bar{y})^2} \qquad \text{Equation 9}$$

Since for any set of data the $\Sigma(y\ \ \bar{y})^2$ term is not dependent on the form of the calibration curve function or the coefficients, the value of (1-r^2) will be directly proportional to the unweighted residual variance as defined in Equation 6.

It becomes apparent that for an average calibration, the coefficient of determination calculated will not provide an optimum measure of error as r^2 applies only to an unweighted least squares determination. The %RSD on the other hand is only meaningful as a measure of error when applied to an average calibration. A generalized indicator of error, *Percent Relative Standard Error (%RSE),* which can be applied to any form of weighted regression function is derived similarly to %RSD making adjustment for the degrees of freedom in the relationship by replacing the *n - 1* factor with *n - p* where *p* is an integer equal to the number of coefficients as defined in Equation 10.

%RSE is equivalent to %RSD when calculated for the average. In Figure 6 the least squares line derived using (1/concentration^2) weighting is compared to the average line and the unweighted least squares line for the same data set used in the previous figures. In this example the elimination of the zero point is responsible for an increase in the %RSE for the weighted line (*p* = 2).

$$\%RSE = 100x\sqrt{\frac{\sum_{i=1}^{n}\left[\frac{\hat{y}_i\ \ y_i}{y_i}\right]^2}{n\ \ p}} \qquad \text{Equation 10}$$

Where:

y_i = Actual response of calibration level
$\hat{y}_i$ = Calculated response from curve
p = number of terms in the fitting equation
(average = 1, linear = 2, quadratic 3)
n = number of calibration points

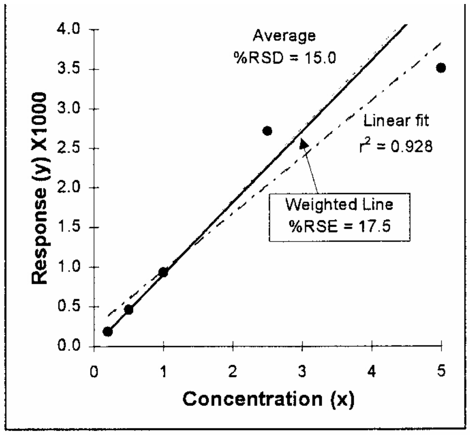


Figure 6

The improved low-end accuracy for this weighted line compared to the unweighted regression line is shown in Table 2. Concentrations measured close to the lowest calibration point would be reported with values approaching 100% lower by using an unweighted linear calibration as compared to the weighted curve.

Table 2

	% Error (calculated - True)	
Concentration	Weighted	Unweighted
0.2	1.7	109
0.5	1.2	29.9
1.0	2.7	2.8
2.5	16.7	25.1
5.0	28.7	8.9

Only recently, in the update to SW-846 method 8000B and also in a draft of guidance for development or modification of water methods[7] has the EPA recognized the importance of considering weighting in calibration calculations. These documents do not, however provide options for evaluating weighted regression fits. The coefficient of determination (COD) used in method 8000B for evaluating polynomial curves is "weighted" only to adjust for the degrees of freedom in the fitting equation and does not provide a measure of error which is suitable for regression curves derived with error weighting.

Non-Linear Calibration

While it is reasonable to use the simplest mathematical relationship, which gives acceptable accuracy, it should not always be assumed that an average or linear curve is preferred. Some detector systems commonly used in the environmental laboratory are inherently non-linear. As an example the electron capture detector (ECD) commonly utilized for its sensitivity to chlorinated pesticides and herbicides can for most analytes provide calibrations which are linear over a 20X concentration range. It is often difficult to optimize detector conditions for multiple analytes with widely varying electron affinities and even under ideal conditions many ECD detectors show linearity within 20% RSD only over a narrow concentration range. The calibration data plotted in Figure 7 was curved for enhanced accuracy over a 32X range by applying a quadratic fit. While the %RSD for the average was not acceptable at 44.9% the quadrati curve gives a %RSE of only 3.7%.

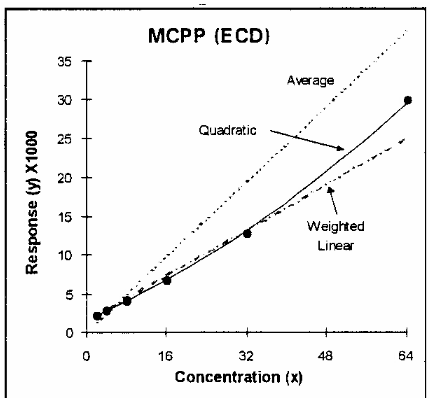
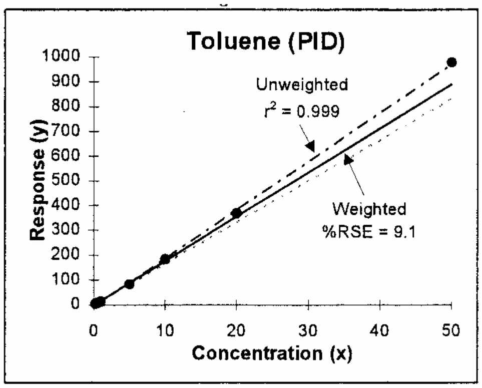


Figure 7

In lieu of higher order curve fitting the approach often defaults to reducing the calibration range, which normally requires re-analysis of some or all calibration points as well as increasing the number of sample dilutions, both of which will add to the cost of the analysis without necessarily providing significant improvement in quality. A simple recalculation of the curve parameters based on a quadratic fit allows the full concentration range of the calibration data to be utilized with improved accuracy. The use of second or higher order curves should not be applied simply to achieve minor improvements in the %RSE that will allow an otherwise unacceptable curve to be used. Justification for higher order calculations should be based primarily on an understanding of the performance characteristics of the detector or the method. The use of higher order curve fitting should also not be substituted for proper instrument maintenance, nor should an effort be made to extend calibrations beyond the detector saturation level.

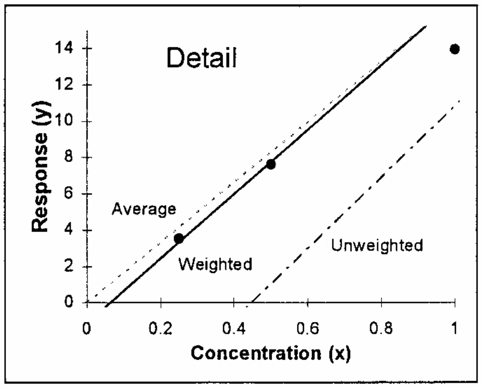
Evaluation of Calibrations

Whenever possible, data evaluation should be performed against rigid criteria that will prevent any tendency for analyst bias to affect reported results and allow automated data validation processes to be implemented. In a production-oriented laboratory setting, visual examination of every calibration curve is not routinely performed. Rather curves are evaluated against calculated criteria only. Modern data systems allow regression parameters to be calculated with very little analyst effort. Although the %RSE calculation is not commonly provided it can usually be implemented either in a user function or by exporting the results to a spreadsheet.



The behavior of the calibration curve near the reporting limit should also be a primary consideration for environmental methods. According to the proposed update to SW-846 method 8000B, data should be considered unreliable for instrument response less than 3 times the y-intercept from the curve if the value is positive, or less than the concentration calculated from zero response if the y-intercept is negative. The use of weighted curve fitting will greatly reduce the possibility that the intercept exceeds these limits. The unweighted line in Figure 8a appears to provide a very good fit to the data with r^2 = 0.999. The expanded view near the low end of the calibration shown in Figure 8b clearly demonstrates the improved fit for the weighted line.

Figure 8a



Recommendations for the minimum number of data points needed to prepare a calibration vary from one to fifteen depending on the method and the order of the fitting equation. Normally five points are considered adequate for linear curves. Some problems may be corrected by elimination of data points from the calibration calculation. This should only done if they are either the highest or lowest concentration and the number of points remaining meets the minimum requirements of the method. The analyst should also be aware that removing the low point might adversely affect the reporting limit, as quantitation must not be performed outside the concentration range of the calibration.

Figure 8b

When second order curves are evaluated, the acceptability should include an evaluation of the curve inflection points. In Figure 9, the quadratic curve (solid line) provides a significant improvement in %RSE over the weighted least squares line (dashed). However, the *y*-value of the curve inflection for this line is below the response of the highest data point, thus quantitation near the upper end of the calibration range could give erroneously high results.

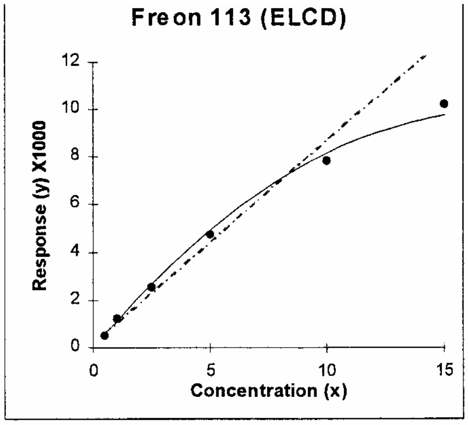


Figure 9

As a rule, all points in the calibration curve should demonstrate a consistent relationship between concentration and response (response increases with increasing concentration). According to SW-846 method 8000B *"... the curve must be continuous, continuously differentiable and monotonic over the calibration range."*

Summary

The correlation coefficient as a criterion for evaluating regression curves does not apply to weighted regressions that are necessary for accurate low concentration reporting of environmental data. The correlation coefficient is also not consistent with the %RSD criterion used to evaluate average curves, often leading to calibration data that is not acceptable for a linear regression based on the correlation coefficient but does meet %RSD criterion of an average calibration.

The Percent Relative Standard Error (%RSE) provides an improved criteria for evaluation of calibration curves in environmental laboratory methods. The advantages of this approach are as follows:

- All curve types can be calculated with the same (1/concentration^2) weighting applied, This places emphasis on relative error with improved accuracy at concentrations near the reporting limit.

- The %RSE criterion is consistent for evaluation of all curve fitting types. Interpretation of acceptability for calibration curves is simplified with the same criterion applied to all curve types and no conflicting criteria.

- The most appropriate curve fitting model can be applied to each set of calibration data with evaluation criteria between different curve types directly comparable.

The evaluation of all calibration data should include, as a minimum, the following checks:

- %RSE < maximum limit
- concentration level of low standard ≤ reporting limit
- low point intersection values < reporting limit
- Number of calibration levels meets method requirements
- All points must be monotonically increasing
- Also for second or higher order curves inflection points should not be within the calibration range

With the widespread availability of powerful computer hardware and software in the laboratory, it is unnecessary to sacrifice data quality for the sake of simplification. Analysts should be familiar with the productivity and quality benefits of least squares curve-fitting algorithms. Clients and regulators must understand the importance of weighted curve fitting and the need for complete and consistant evaluation criteria, which will provide high quality results for the lowest cost.

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QUALITY CONTROL PROTOCOL FOR ANALYSIS OF DRUGS AND EXPLOSIVES USING ION MOBILITY SPECTROMETRY

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Ion mobility spectrometry (IMS) is widely used as a screening tool in the detection of contraband drugs and explosives. It is also gaining popularity as a semiquantitative instrument used in the research of these and other compounds, including hazardous environmental contaminants. We have successfully used IMS in studies involving cocaine and TNT, and have developed a quality control protocol to assess and ensure the quality of our data. This protocol employs cocaine hydrochloride as the reference standard in the positive mode and trinitrotoluene (TNT) as the reference standard in the negative mode. A five point calibration curve was generated for each of the reference compounds in order to determine a concentration level suitable for quality control (QC) check solutions. We have established peak amplitudes and reduced mobility constant (K_0) for the QC check solutions that must be met each day before proceeding with analyses. Any deviation from these criteria requires assessment of the problem and appropriate corrective action. We have found this procedure helpful in maintaining data quality and in providing an early indication of potential problems.

REFERENCE MATERIAL FOR THE ANALYSIS OF METALS IN SLUDGE

Stuart J. Nagourney, Nicholas J. Tummillo, Jr., John Birri, Kenneth Peist, Bruce MacDonald and Jean S. Kane

INTRODUCTION

New Jersey Department of Environmental Protection (NJDEP) regulations limit the levels of discharged toxic substances in sludge effluents by sewage treatment plants. Once maximum contaminant levels are established, they become part of the facility's operating permit. When chemical analyses indicate that these permit levels are exceeded, the NJDEP has statutory authority to assess significant monetary penalties.

Sludge samples vary widely in their physical and chemical composition, ranging from liquids with low dissolved solids content and small quantities of organics and metals, to multi-phase samples and cakes with solids contents often greater than 50 % and concentrations of metals and other constituents at percent levels. Since permit limits for metals are based on the amount leached during mineral acid digestion, these acid extractable concentrations, rather than total concentrations, are the values of interest. With several options for methods of sample preparation and measurement being proposed by State and Federal agencies, comparability of data among methods is a critical issue. Reference materials of similar matrix and composition to the various sludge matrices, and having known metal levels with defined uncertainties, are essential to insure that an accurate assessment of the data being generated is made,

To expand the utility of existing environmental SRMs, NIST has initiated efforts provide data on the acid-extractable levels of metals in selected new solid sample environmental SRMs. A recent paper by these authors described a collaborative project among the NJDEP, USEPA, Region II Technical Support Branch and NIST to develop sludge reference materials from domestic and industrial sources having reference values for their acid-extractable metals content. The study was successful for the domestic material, resulting in the derivation of reference values for EPA acid-extractable methods as part of SRM 2781, Domestic Sludge. The addendum to SRM 2781 contains leachable mass fractions for 14 metals and compares the leach recoveries to total metal concentrations obtained separately. This paper discusses the analysis of the industrial sludge material, NIST SRM 2782.

EXPERIMENTAL

Reference Samples

The candidate industrial sludge reference material SRM 2782, was prepared from more than 100 kg of electroplating waste supplied by AT&T Bell Laboratories, Murray Hill, NJ. This material was shipped to NIST, wherein it was freeze-dried, processed, radiation sterilized and homogenized by contractors according to procedures used to prepare United States Geological Survey and NIST geological reference materials. Samples were aliquotted and shipped to the participating laboratories, the NJDEP Bureau of Radiation and Inorganic Analytical Services (BRIAS) and USEPA, Region II, Technical Support Branch, for chemical analysis.

Sample Preparation

The NJDEP used open vessel hot plate digestion (NJDEP Method 100) for all of their acid digestions. The USEPA used open vessel hot plate digestion (USEPA Method 3050) for the industrial sludge and Method 3050 and closed vessel microwave digestion techniques (USEPA Method 3051) to prepare the domestic sludge for measurement. EPA prepared two sets of samples using microwave digestion, one without and one with HCl.

Instrumentation

The NJDEP used a Perkin-Elmer (PE) Model 5000 atomic absorption spectrometer (AAS) for its flame atomic absorption (FAAS) metal measurements. A similar unit, equipped with a PE Model 500 furnace and a PE AS-50 autosampler, was used for the graphite furnace atomic absorption (GFAAS) measurements. The NJDEP also employed a Thermo-Jarrell Ash Model 25 sequential inductively coupled plasma emission spectrometer (ICPOES) for some of its metal determinations. The USEPA used a CEM Model MDS-2000 microwave digestion system for some sample preparations and a Thermo Jarrell-Ash Model 61 Simultaneous ICPOES and a PE 5100 GFAAS, equipped with a model AS-600 furnace and AS-60 autosampler for its metal determinations. The USEPA performed the metals measurements by either simultaneous ICPOES and GFAAS, using one technique per metal. The NJDEP employed more than one technique to measure most of the metals.

Sample Processing

Each laboratory analyzed its own digests by one or more instrumental methods. Once completed, the two laboratories exchanged extracts and conducted another series of measurements using the same techniques.

RESULTS AND DISCUSSION

Developing "reference” values for the composition of real environmental samples requires inclusion of random errors of measurement and any systematic bias which might be inherent in the method(s) employed to estimate the true value. Issues such as the method of measurement, the complexity and composition of the sample matrix and the concentration and heterogeneity of the analytes all contribute to the overall uncertainty. While relative uncertainties of -20% to + 20% are expected when EPA methods such as FAAS, GFAAS and ICPOES are applied to nonaqueous media, reference values based upon these methods are still useful as confirmation of results of environmental monitoring such as the analysis of sludge effluents from treatment plants.

Current Results for Industrial Sludge

The initial set of analyses performed on NIST SRM 2782 yielded poor agreement between the two laboratories. For the most recent series of tests, the precision of the 6 aliquots of NIST SRM 2782 ranged from 0.2 % to 2.0 % for all elements measured by both participating laboratories. There is no discernable change in the level of precision of the replicate measurements obtained in the earlier and later studies Table 1 compares the results obtained by both laboratories in the initial ('94) and most recent ('96) studies. There is no discernable pattern in the NJDEP data from 1994 to 1996; the more recent series of USEPA results are generally higher than those obtained previously. Differences between the grand means of all results obtained for each element by the two laboratories for the more recent set of measurements were within 6% for 6 elements and 10% for 12 of the 17 metals studied; 2 others were within 12 %. Cd, Cr and K were the only elements outside this range,

Analysis of Variance (ANOVA) can be utilized to evaluate whether the individual element means obtained by the two laboratories for each element, generated by different methods of sample preparation and analysis, are statistically significant. As shown in Table 2, for the 14 metals where agreement between the grand means was within 12 %. ANOVA analyses, as shown by the F value (ratio of variance between data sets to the variance within a data set) and P value (measure of the probability the actual sample set fell within hypothetical frequencies for infinitely large data populations) showed that the means obtained by the two laboratories agreed within specified tolerances for 11 of the 14 metals; the exceptions being Ba, Cr and Mn. This serves as further corroboration to the extent of the agreement between the results.

The USEPA obtained good results for 14 metals where extractions were obtained by both Method 3050 (hot plate digestion) and Method 3051 (microwave digestion), with analyses performed by ICP-OES. Agreement is within ± 6 % for all metals studied but Na and K; with a range in bias from - 4.8 % for Al to +5.2 % for Zn. These results are shown in Table 3. The values for the alkali metals Na and K are approximately 30-40 % higher for the microwave technique. When the t-test for means assuming unequal variance is applied, for 6 metals (Ba, Ca, Cu, Mn, Ph and Zn), the differences between the calculated means obtained by each method were statistically significant. However, these detected differences are relatively small, especially when compared to the control limits assigned to acid-extractable analytes measured in non-aqueous media. All standard deviations are ± 2 sigma.

Comparison of Leachable Concentrations for Domestic Sludge and Industrial Sludge

The addendum to the Certificate of Analysis for NIST SRM 2781, domestic sludge compares the % leach recoveries of selected metals with the values obtained for their total mass fractions. For elements where leachable metal results were obtained from both the USEPA and NJDEP laboratories, a ratio of leachable metal concentration to total metal concentration (obtained by NIST) was calculated. For the domestic sludge these ratios were between 0.82 and 0.96 for 9 out of 11 elements; only Al (0.50) and Cr (0.71) were below this range. Preliminary values supplied by NIST for the industrial sludge material shows a different pattern; for the 14 elements for which such data is available, only 6 have ratios of leachable to total that are greater than 0.80. Na, K, Mg, Al have ratios below 0.20, the ratio for V is 0.21, Ba and Ni are 0.60 and 0.62 respectively, while Ca is 0.72. Only certain transition elements (Cu, Ph, Zn, Mn, Fe and Co) have leachable/total ratios for the industrial sludge that are greater than 0.80. The results are summarized in Table 4. Note that for the industrial sludge all of the ratios for the alkali and alkaline earth metals as well as Al are 0.72 or below. While the reasons for the specific analyte-matrix interactions are uncertain, it is apparent that the more complex nature of the industrial sludge plays a key role in how much metal is leached by the regulatorily-approved digestion methods, and that the amount that leaches varies significantly by element and group. This issue must be considered when evaluations of leachable metal concentrations are made for environmental assessment and policy considerations.

Table 1. Industrial Sludge - Grand Means

Element	Mean DEP'94	Mean EPA'96	Mean DEP'94	Mean DEP'96	DEP/EPA ‘96
Al	1502 ± 43	1587 ± 107	1380 ± 50	1528 ± 46	1.038
Ba	150 ± 1	161 ± 11	132 ± 4	144 ± 4	1.118
Ca	4687 ± 470	4950 ± 144	4320 ± 141	4685 ± 151	1.056
Cd	4.0 ± 0.1	11.4 ± 3.0	15.4 ± 0.8	2.3 ± 0.1	-
Co	70.0 ± 6	51.6 ± 7	54.4 ± 2	56.0 ± 3	0.921
Cr	79.8 ± 1	76.7 ± 4	55 3 ± 2	58.3 ±1	-
Cu	2485 ± 146	2459 ± 37	2270 ± 53	2420 ± 42	-
Fe	255020± 17000	256600± 2300	232000±5600	253000±14000	1014
K	116±1	121 ±2	58.9 ±6	78.6 ±21	-
Mg	508±37	498 ±69	441 ±17	470± 15	1.059
Mn	274 ±13	274 ±7	224 ±7	247±7	1.109
Na	2430± 18	2431 ±20	2000 ±123	2573 ±307	0.945
Ni	125±2	95.5 ±6	908±2	96.1 ±4	0.994
Pb	581 ±18	558± 9	519 ±30	553 ±22	1.010
V	23.2± 1	17.5 ±2	20.6 ±1	15.9± 1	1.100
Zn	1266 ±31	1181 ±59	1170±21	1158 ±71	1.019

Table 2. Industrial Sludge - ANOVA Analyses

	F	P
Al	0.82	0.38
Ba	33.9	0.00
Ca	1.73	0.22
Co	0.25	0.62
Cr	3.67	0.00
Cu	0.51	0.49
Fe	4.09	0.06
Mg	2.25	0.14
Mn	69.6	0.00
Na	0.06	0.81
Ni	4.20	0.09
Pb	3.52	0.09
V	2.32	0.14
Zn	0.07	0.79

CONCLUSIONS AND RECOMMENDATIONS

Reference values have been derived for the leachable concentration of 14 metals in an industrial sludge standard reference material (NIST SRM 2782). Both open vessel hot-plate acid digestion (NJDEP Method 100 or USEPA Method 3050) or microwave digestion (USEPA Method 3051) are appropriate methods for sample preparation of these materials and the leachable concentrations may be measured by either FAAS, sequential or simultaneous ICPOES. This information supports the application of performance-based methodology since there are several combinations of sample preparation and measure- ment systems that can achieve similar results. Following complete statistical review by NIST, sludge Standard Reference Materials from both domestic and industrial sources-will be commercially available. Reference values for their acid extractable metals content and associated uncertainties will be provided to support the quality assurance of sludge metal measurements. Analyses of these SRMs should be required as part of a POTW's compliance data submitted to regulatory agencies Such as the USEPA and NJDEP. It is also recommended that these materials become part of any future laboratory certification program for sludge effluents.

Table 3. Industrial Sludge - Method Comparison

Element	Method 3050		Method 100		3050/100
	Mean	SD	Mean	SD	
Al	1520	18	1540	8	0.987
Ba	148	2	144	1	1.027
Ca	4870	58	4720	34	1.032
Co	58.5	0.9	57.0	0.9	1.026
Cr	57.9	0.6	58.2	2.4	0.994
Cu	2500	37	2420	45	1.033
Fe	260000	4500	236000	1100	1.102
K	72.4	11.8	80.1	1250	0.904
Mg	470	5	490	7	0.959
Mn	256	3	246	3	1.041
Na	2300	39	2470	60	0.931
Ni	99.6	3.7	95.1	1.1	1.047
Pb	545	6	524	13	1.040
Zn	1210	15	1210	11	1.000

Table 4. Domestic Sludge -Recoveries and Comparisons w/Certificate

Element	Domestic Sludge Ratio: Leachable / Total	Industrial Sludge Ratio: Leachable / Total
Ag	0.88	-
Al	0.50	0.11
Ba	-	0.60
Cd	0.86	-
Ca	0.93	0.72
Co	-	0.82
Cr	0.71	-
CU	0.96	0.94
Fe	0.87	0 95
K	-	0.02
Pb	0.91	0.97
Mg	0.82	0.18
Mn	0.82	0.86
Na	-	0.19
Ni	0.90	0.62
V	-	0.21
Zn	0.88	0.93

- Only NJDEP or USEPA leachable results were available, mean values between the two laboratories was not computed.

PERSPECTIVES ON DIOXIN ANALYSIS

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Dioxin analysis is very complex. Many people do not understand how dioxin analysis is performed within a laboratory or how to validate the data when they receive it. Through my technical assistance to internal and external customers concerning dioxin analysis, it has become clear they do not understand and are afraid to understand the

methodology of dioxin analysis. Prior to validating PCDD/PCDF data, it is imperative to have complete knowledge of the method used. The purpose of this paper is to try and simplify dioxin analysis. To break the analysis into understandable pieces and to compare it to other organic analyses. The basis for the Dioxin/Furan analysis is Selected Ion Monitoring (SIM) Gas Chromatography/Mass Spectrometry (GC/MS). The objective of this paper is to explain SIM GC/MS and isotope dilution for the average nonchemist. The advantages and disadvantages of using isotope dilution and SIM over the "routine" organic methods will be discussed.

INTERPRETATION OF GROUND WATER CHEMICAL QUALITY DATA

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ABSTRACT

Ground water is sampled to assess its quality for a variety of purposes. Whatever the purpose, it can only be achieved if results are representative of actual site conditions and are interpreted in the context of those conditions.

Substantial costs are incurred to obtain and analyze samples. Field costs for drilling, installing, and sampling monitoring wells and laboratory costs for analyzing samples are not trivial. The utility of such expenditures can be jeopardized by the manner in which reported results are interpreted as well as by problems in how samples were obtained and analyzed. Considerable attention has been given to standardizing procedures for sampling and analyzing ground water. Although following such standard procedures is important and provides a necessary foundation for understanding results, it neither guarantees that reported results will be representative nor necessarily have any real relationship to actual site conditions. Comprehensive data analysis and evaluation by a knowledgeable professional should be the final quality assurance step, it may indeed help to find errors in field or laboratory work that went otherwise unnoticed, and provides the best chance for real understanding of the meaning of reported results.

The focus of this paper is on the interpretative part of the process. Although formal interpretation necessarily comes late in a project, when data have been generated and the report is being written, it will be most useful if relevant elements can be integrated into the project from the beginning. When this is done, it increases the likelihood of achieving project objectives as well as understanding the data. To facilitate interpretation, the following steps should be included:

1. Collection, analysis, and evaluation of background data on regional and site-specific geology, hydrology, and potential anthropogenic factors that could influence ground water quality and collection of background information on the environmental chemistry of the analytes of concern.
2. Planning and carrying out of field activities using accepted standard procedures capable of producing data of known quality.
3. Selection of a laboratory to analyze ground water samples based on careful evaluation of laboratory qualifications.
4. The use of appropriate quality control/quality assurance (QC/QA) checks of field and laboratory work (including field blank, duplicate, and performance evaluation samples).
5. Comprehensive interpretation of reported analytical data by a knowledgeable professional. The analytical data must be accompanied by appropriate QC/QA data, be cross-checked using standard water quality checks and relationships where possible, and be correlated with information on regional and site-specific geology and hydrology, environmental chemistry, and potential anthropogenic influences.

Application of this sequence *of* steps and their importance in interpretation of ground water quality data are discussed in this paper. The discussion includes several illustrative case examples.

INTRODUCTION

There area number of reasons we might want to know about groundwater chemical quality. For example, we might be interested in using an aquifer as a source of water today or we may want to ensure that current practices haven't caused contamination so that ambient ground water quality remains legally acceptable whether or not it is used in the future. At first glance, you'd think that obtaining and interpreting ground water quality data would be a fairly straight forward exercise. Simply follow the usual scientific approach: (1) take a sample; (2) analyze it; and (3) compare analytical results to a set of criteria. However, obtaining reliable data and properly interpreting them turns out to be more complicated than that; even in the relatively simple case of surface water. When it comes to ground water, everything seems more complex.

To begin with, obviously, with ground water you can't just go down to the stream and get a sample. Because ground water is underground, you need to do more preparation in advance of sampling. This involves obtaining background subsurface information and an access point. Such information will be helpful, both in planning how to obtain a sample as well as in interpreting analytical results when they become available. Whether you use a standard monitoring well, direct push technology, or something else, getting access to sample isn't always easy and can influence the quality of the sample obtained. There are also a number of potentially confounding factors with regard to the next step of the process, laboratory analysis. Sample quality can change between the time a sample is obtained and the time it is analyzed and, even if it doesn't, the overall reliability of laboratory results is not the sure thing many people assume it is. Finally, selection of appropriate criteria to compare data to may not always be straight-forward. Relevant criteria may either not exist or be incomplete.

Comprehensive data interpretation by a knowledgeable professional should be the final quality assurance step of any project involving ground water quality data. It may indeed help to find errors in field or laboratory work that went otherwise unnoticed and provides the best chance for real understanding of the meaning of reported results. Proper project planning should prepare for this final step by obtaining relevant information early on and including relevant data collection into field segments of the project. The following steps must be integrated into and carried out throughout the project to facilitate final interpretation:

1. Collection, analysis, and evaluation of background data on regional and site-specific geology, hydrology, and potential anthropogenic factors that could influence ground water quality and collection of background information on the environmental chemistry of the analytes of concern.
2. Planning and carrying out of field activities using accepted standard procedures capable of producing data of known quality.
3. Selection of a laboratory to analyze ground water samples based on careful evaluation of laboratory qualifications.
4. The use of appropriate QC/QA checks (including field blank, duplicate, and performance evaluation samples).
5. Comprehensive interpretation of reported analytical data by a knowledgeable professional.

The analytical data must be accompanied by appropriate QC/QA data, be cross-checked using standard water quality checks and relationships where possible, and be correlated with information on regional and site-specific geology and hydrology, environmental chemistry, and potential anthropogenic influences.

BACKGROUND INFORMATION

Background information serves several functions: (1) it facilitates obtaining access to sample groundwater; (2) it provides guidance regarding selection of appropriate sampling methods and analytical variables; (3) it places ground water quality data into context; and (4) it provides a quality assurance check. The following background information is necessary to fulfill these functions: (1) regional and site-specific geology; (2) regional and site-specific hydrology; (3) information on the environmental chemistry of variables of concern to the project; and (4) broad information on potential anthropogenic influences including site conditions and possible contaminant sources. The latter includes not only those conditions which may have impacted ground water, but those which could have influenced sample quality as a result of installation and testing of monitoring wells or otherwise during the sampling process. For example, shallow contamination can be carried down into a deeper aquifer during field work and airborne chemicals may cause trace contamination of ground water samples if they enter an open borehole, monitoring well, or sample being placed into a container.

FIELD PROCEDURES

Access Points

The nature of subsurface conditions will influence the type of access point that is possible. Sample quality will also be impacted by the type of access point selected. Commonly used ground water access points include: (1) monitoring wells; (2) wells or piezometers installed for other purposes; and (3) direct push technology.

The nature of the access point has, in particular, a relationship to the level of total suspended solids (TSS) likely to be present in samples. TSS levels would be expected to be relatively high in samples obtained using direct push technology and low in samples obtained from a water supply well. Assuming proper design and installation (including development), TSS levels in samples obtained from monitoring wells will normally be low except where fine-grained materials are screened. However, development is something that is often neglected or treated in a pro-forma manner when monitoring wells are installed. Additional development, as opposed to routine purging, may also be required when there are long periods between sampling events. This is illustrated in Table 1, showing results for inorganic variables in unfiltered samples from a well that was properly developed prior to initial sampling but was not redeveloped when sampled again after two years.

Sampling Methods

Available sampling methods are often constrained by the type of access point utilized. Since they will have a direct bearing on sample quality, the sampling methods used must be taken into account in planning sampling events and in interpretation of the data obtained. This category includes consideration of both field equipment and procedures. For example, regulatory agencies are more frequently requiring analysis of unfiltered samples. This may introduce substantial variation into the process, particularly for inorganic variables.

Sample Handling and Preservation

The order of sampling, type of container, and sample preservation method utilized can affect the quality of samples analyzed in the laboratory. As discussed further below, U.S. Environmental Protection Agency (USEPA) specified sample preservation methods and maximum allowed holding times do not always ensure sample quality will not change between the field and laboratory analysis.

Field Analysis/Observations

Reliable sample preservation methods do not exist for some water quality variables. In other cases, field measurements carried out for other purposes (i.e., well purging) are routinely available and preferable (e.g., to laboratory analysis for the same variable) or field observations can be made that provide useful information otherwise lost if not recorded at the time. USEPA requires field analysis (by specifying immediate analysis) for only five variables: (1) chlorine residual; (2) pH; (3) dissolved oxygen (by probe); (4) sulfite; and (5) temperature.

The validity of some USEPA maximum holding times and preservation combinations is questionable. For example, although USEPA recognizes that pH and dissolved oxygen levels may change substantially if not analyzed in the field and therefore requires immediate analysis without holding for them, substantial changes in alkalinity may occur for the same reasons but 14 days holding time is allowed for this variable. Because it is allowed and more convenient, samples are frequently analyzed in the laboratory for alkalinity instead of the field. Similarly, USEPA allows maximum holding times of 48 hours and seven days for color and total suspended solids (TSS), respectively. USEPA also allows seven and 14 days holding time for unacidified and acidified volatile aromatic compounds, respectively. Both color and TSS may change substantially in samples over these allowed time frames and research has shown both substantial loss of volatile aromatic compounds in less than seven days in unacidified samples and that substantially greater holding times than 14 days are appropriate for many compounds when samples are acidified.[1]

When sampling ground water, field analysis should routinely occur for the purge variables conductivity, pH, and temperature, using appropriate equipment operated, calibrated, and maintained in accordance with manufacturer recommendations. The following field observations related to sample quality may also be made: (1) color; (2) odor; and (3) turbidity. Although this information is essentially "free" for the taking, it is often not recorded. In particular, the latter observation can provide at least a qualitative indication *of* the presence of TSS and their possible effect on inorganic variables. The difference that filtering makes in reported concentrations of many inorganic variables when unfiltered samples contain high solids concentrations is substantial and readily demonstrated with split samples.

LABORATORY ANALYSIS

Too often, the analytical laboratory for a project is selected on the basis of cost only. Such cost savings may prove to have been very expensively purchased if quality isn't also delivered. Laboratory qualifications should be carefully researched in advance of selection. This can be done by such things as reviewing historic results on performance evaluation samples, auditing the facility, submitting performance evaluation samples, and checking references. Checks should continue throughout the project with the appropriate use of blank, duplicate, and performance evaluation samples.

Unfortunately, no laboratory is perfect. Even the better laboratories often get some wrong answers when analyzing USEPA performance evaluation samples. These are in a relatively clean matrix, without the kinds of interferences that can complicate real world samples, and are being analyzed under test conditions. A laboratory would be foolish not to make its best effort on these samples. You can expect somewhat lower quality with regard to samples being routinely analyzed for the average client. Routine QC/QA and data validation practices are not the complete answer to data quality. In particular, the latter usually don't include various data cross-checks or take into account what is known about site conditions. In the worst case, laboratory reported analytical results can be more artifacts of the sampling and analysis process than representative of ambient ground water quality.

There are a number of factors which can influence laboratory results. But even when analytical laboratories are performing well, it should be recognized that: (1) at best, they can only analyze samples in the condition received; and (2) standard limits of precision and accuracy allow considerable variation. As noted above, a number of factors may result in samples reaching the laboratory which are less than representative of site conditions. Even when laboratory QC/QA requirements are met, the level of allowed variation limits the conclusions which can be based on laboratory data. USEPA Superfund acceptance criteria for percent recovery of matrix spikes (MS) and laboratory control standards (LCS) are shown in Table 2.[2,3]

Data reported by laboratories should be carefully reviewed or "validated" before being utilized. USEPA national functional guidelines for data review under Superfund are an example of typical validation guidelines. These specify a number of checks intended to assure that correct procedures were followed (e.g., holding times, calibration, blanks, matrix spikes and spike duplicates, and laboratory control standards). Although this type of review is useful, it is important to realize its limitations. The standard conclusion one consulting company uses after a successful validation process contains the statement that "the data collected during this investigation are valid as qualified for use in representing Site conditions and for use in risk assessments."[4] Since the validation process referred to doesn't take relevant site information or available data cross-checks into account, such a statement goes too far. Neither is it necessarily correct.

CASE EXAMPLES OF INTERPRETING GROUND WATER DATA

Organic Contamination at a Superfund Site

Trichloroethylene (TCE) groundwater contamination was recognized at a Superfund site. The presence of other halocarbons associated with TCE degradation, notably cis-1,2-dichloroethylene (c-1,2-DCE) and vinyl chloride, was also recognized. However, the potentially responsible party (PRP) claimed the TCE originated elsewhere and was part of a wider regional problem involving a number of sources and contaminants. Site work performed by the PRP in 1996 identified a variety of other compounds in samples from relatively deep wells drilled using air rotary equipment. The compounds reported in various samples fell within the following categories:

1. Volatile organic compounds (VOCs) -
    a. Halocarbons including TCE and TCE degradation products.
    b. Petroleum hydrocarbons, including aromatic compounds (e.g., xylenes).
    c. Trihalomethanes, particularly chloroform and bromodichloromethane.

2. Semivolatile organic compounds (SVOCs) -
    a. Petroleum hydrocarbons (benzoic acid and naphthalene).
    b. Phenol and other phenolic compounds.
    c. Phthalates, particularly bis(2-ethylhexyl)phthalate.

Review of these data indicated that other interpretations were much more likely. Among the reasons the data were suspect were the following:

1. With the exception of halocarbons, most of the compounds involved had not been reported in samples from shallow wells previously drilled using hollow-stem augers. Contamination in such cases generally moves from surface or near-surface sources downward. Furthermore, the concentrations involved were generally low and appeared to be randomly distribution rather than in a pattern suggesting any relationship to possible sources.

2. Air rotary drilling is a possible source of petroleum hydrocarbon and phenolic compound contamination.

3. Some of the boreholes had been left open to the atmosphere for substantial periods of time (i.e., on the order of

months) after drilling before monitoring wells were installed in them. The ones open the longest were also adjacent to an Interstate Highway. Petroleum hydrocarbons have been identified in vehicle emissions and ambient urban air.[5] Research has also indicated the potential for petroleum hydrocarbons and phenolic compounds in urban air to be transported into ground water.[6,7]

4. PRP consultants had not decontaminated at least some downhole equipment (particularly water level indicators) when used between boreholes or between monitoring wells. This may cause cross-contamination.

5. THM contamination is common in chlorinated tap water from surface sources, but unusual in ambient ground water. Thousands of gallons of chlorinated tap water from a surface source known to contain substantial concentrations of trihalomethane compounds had been introduced into most of the boreholes as a part of the testing program during field work.

6. Phthalates are recognized by USEPA as a common SVOC laboratory contaminant.[8]

7. Background regional information strongly indicated the PRP was the source of halocarbon contamination and that there was no other more widespread regional problem involving halocarbons or other compounds.

Resampling in 1997 provided further confirmation of this interpretation. Data for the 19 wells sampled in both years are shown in Table 3 (parts a and b). With the exception of a reduced number of low concentration hits for phthalate compounds (which are recognized as common laboratory contaminants) and, in one case, a trihalomethane compound, only halocarbons were reported in 1997. This indicates that the various other compounds reported in 1996 samples were a transitory impact of drilling, testing, sampling, and analysis rather than regional ground water contamination. This transitory impact dissipated over time as a result of natural mechanisms such as flushing by ambient ground water flow and biodegradation. The change in apparent distribution of halocarbon contamination between 1996 and 1997 apparent from these results may also indicate that shallower contamination was carried downward by intrusive work performed in 1996 and that this also produced a transitory impact on ground water samples.

Ground/Surface Water Relationship at a RCRA Site

Ground water monitoring at landfills and other Resource Conservation and Recovery Act (RCRA) facilities is oriented towards ensuring that a release of contaminants, if it occurs, will be detected. In general, detection monitoring requires that data from wells downgradient of the facility and subject to impact in event of a release be statistically compared to data from upgradient background wells. If the comparison results in a statistically significant difference with a downgradient increase, a release is assumed. However, other regional conditions must be considered if such comparisons are to be useful.

In this case, there is a network of monitoring wells installed up and downgradient of a land treatment unit (LTU) located at a refinery adjacent to a major river. Statistical analysis showed that concentrations of some variables were elevated in downgradient wells and that the elevations were statistically significant. Did this mean that a release had occurred?

A linkage between the river and the adjacent alluvial ground water aquifer would be expected based on general principles. This was confirmed by analysis of two lines of evidence: (1) correlation of ground water elevations with river flow (a surrogate for stage); and (2) statistical analysis of water quality data. Time series plots of ground water elevations versus river flow showed an evident visual correlation, which was confirmed by linear regression analysis. The correlation was best for those wells closest to the river (correlation coefficient of 0.80) and decreased with distance from the river. A comparison of water quality data is supportive. Data indicating central tendency for upgradient monitoring wells and the river are presented for six variables in Table 4. For the three major ions in Table 4, including chloride, river concentrations far exceed those in upgradient ground water. In these cases, statistical analysis shows that concentrations in samples from downgradient monitoring wells are significantly higher than upgradient ground water. The reverse is true for the three elements listed. Their concentrations are higher in upgradient ground water than the river and statistical analysis shows that their levels in downgradient monitoring wells are significantly lower than upgradient.

Inorganic Water Quality at a Superfund Site

Consultants for a PRP at a Superfund site involving a limestone aquifer in the midwest US developed several theories regarding the nature of the aquifer involved based on their interpretation of data for inorganic constituents. Data for alkalinity, aluminum, calcium, iron, silica, sodium, and sulfate were prominent in their interpretation. However, these consultants did not consider relevant site-specific information and admitted they were unaware of the degree of variation that can occur in laboratory analysis of ground water samples that meet acceptance criteria (see Table 2).

A potentially important piece of site-specific information not considered by the PRP's consultants was that most of the borings involved had been drilled considerably deeper than the wells later installed in them. For the wells being installed in such deeper borings, boreholes were first partially filled by pouring in sodium bentonite chips. This occurred for about two-thirds of the relatively deep wells drilled. On the average, approximately one-third of the borehole was filled (i.e., 71 of 221 feet). This process undoubtedly resulted in the introduction of chemicals from the hydrating chips into the water (both as dissolved and suspended solids) as they fell through the water column. Of the analytes relevant to this site, sodium bentonite chips are typically composed of silica and oxides of aluminum, iron, calcium, sodium, magnesium, and potassium (in order of concentration). They also contain a small level of water soluble nitrate. Given the chemistry of silica and calcium and the likelihood that calcium in a limestone aquifer would be expected to already be near saturation, concentrations of these variables would probably not be greatly affected by this. However, concentrations of aluminum, iron, sodium, magnesium, and potassium could be and this appears to have been the case. The potential for this was increased by the fact that, although consultants for the PRP purged three well volumes immediately prior to sampling, they did not develop the monitoring wells after installation.

To evaluate the effect of filling boreholes with bentonite on inorganic ground water quality, monitoring wells sampled both during 1996 (shortly after installation) and 1997 (nearly a year since last sampled) were divided into two groups: (1) bentonite filled (BF); and (2) unfilled (UF). Median data for major cations, major anions, and several other variables grouped into these two categories for both 1996 and 1997 sampling events are presented in Table 5. The 1996 data clearly indicate impact from bentonite filling for most of the variables listed except calcium and silica, BF:UF ratios for sodium, aluminum, and iron indicate nearly an order of magnitude or greater level of enrichment for those variables as a result of bentonite filling. This is also evident in the STIFF diagrams of median grouped data in Figure 1. The STIFF diagram for unfilled wells (Figure 1a) is typical of what would be expected for a limestone aquifer.[9] There are several relatively minor differences between the STIFF diagram for bentonite filled wells (Figure 1b) and unfilled wells (Figure la), but by far the most notable difference is the sodium "bulge" to the lower left of the diagram. The impact of the bentonite appears to have been transitory. With the possible exception of nitrate, the enrichment appears to have been flushed away due to ambient ground water flow by the time wells were resampled nearly a year later. STIFF diagrams for both sets of wells (UF and BF) when resampled in 1997 were similar to each other and the one for unfilled wells in 1996 (Figure 1a).

The PRP's consultants pointed to two aspects of the data to support their interpretation that the aquifer involved was an "open" system (i.e., rapidly recharged from the surface throughout the aquifer): (1) abnormally high concentrations of aluminum and iron in samples from some relatively deep wells (exceeding solubility limits); and (2) lack of any apparent ground water evolution (change in quality along a flow line) between wells at higher elevations and those at lower elevations (a distance of roughly one mile). As discussed above and shown in Table 5, aluminum and iron enrichment appears to have been related to filling boreboles with sodium bentonite chips. Not knowing about this circumstance and since the overlying clay soils involved would be normally expected to be rich in silica as well as aluminum and iron, the consultants interpreting inorganic water quality data for the PRP felt compelled to provide another explanation why silica concentrations were not also enriched when aluminum and iron were. Their explanation was an assertion, without any data, that the soils were lateritic. Lateritic soils develop in hot, wet tropical climates subject to heavy rainfall when the intense chemical weathering that occurs under those conditions removes both soluble materials and much of the silica. Lateritic soils are not characteristic of the temperate climate midwest US.[10] A much more likely explanation for the relative magnitudes of aluminum, iron, and silica has to do with the manner in which samples were taken, preserved, and prepared for analysis. Samples to be analyzed for aluminum and iron are acidified in the field and digested in the laboratory. Since the samples involved were unfiltered, this meant that some particulate aluminum and iron would be included in the measurement. In contrast, samples to be analyzed for silica are not acidified in the field, but are filtered prior to analysis.

With respect to ground water "evolution," this phenomena has generally been documented on a regional rather than a site scale. This may be in part because very substantial "evolution" must occur to be detectable against a background of variation sampling and analysis introduced variation as well as environmental variation. For an extreme example, using the acceptance criteria of 75 to 125 percent recovery for matrix spike samples (see Table 2), a sample having a true value of 100 mg/L of calcium could be reported to have either 75 or 125 mg/L. Although the higher of these two numbers is 67 percent greater than the low number, either one would be within acceptance criteria. With enough sampling events and statistical analysis of data, it might be possible to detect an "evolutionary" change within acceptance criteria boundaries (e.g., a change from 50 to 65 mg/L along the flow path); however, the possibility of seeing this change with a single set of samples appears slim when so much variation is acceptable.

SUMMARY AND CONCLUSIONS

Comprehensive data interpretation by a knowledgeable professional should be the final quality assurance step of any project involving ground water quality data. It may indeed help to find errors in field or laboratory work that went otherwise unnoticed and provides the best chance for real understanding of the meaning of reported results. Proper project planning should prepare for this final step by obtaining relevant information early on and including relevant data collection into field segments of the project. The following steps must be integrated into and carried out throughout the project to facilitate final interpretation:

1. Collection, analysis, and evaluation of background data on regional and site-specific geology, hydrology, and potential anthropogenic factors that could influence ground water quality and collection of background information on the environmental chemistry of the analytes of concern.
2. Planning and carrying out of field activities using accepted standard procedures capable of producing data of known quality.
3. Selection of a laboratory to analyze ground water samples based on careful evaluation of laboratory qualifications.
4. The use of appropriate QC/QA checks (including field blank, duplicate, and performance evaluation samples).
5. Comprehensive interpretation of reported analytical data by a knowledgeable professional.

The analytical data must be accompanied by appropriate QC/QA data, be cross-checked using standard water quality checks and relationships where possible, and be correlated with information on regional and site-specific geology and hydrology, environmental chemistry, and potential anthropogenic influences.

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Table 1. Effect of Monitoring Well Development[1]

Variable	Spring 1994[2]	Summer 1996[3]
Calcium	92.	104.
Chloride	43.	58.3
Iron	0.08	5.53
Magnesium	2.4	2.84
Manganese	0.069	0.13
Potassium	ND	533
Sodium	5.8	6.38
Appearance	Clear	Turbid

1. Concentrations in mg/L. ND means non-detect at 1 mg/L.
2. New well developed and purged prior to sampling.
3. Well unused for two years. Three well volumes purged prior to sampling.

Table 2. USEPA Superfund Acceptance Criteria

Variable (USEPA Method)[1]	MS[2]	LCS[2]
Elements (6010)	75-125	80-120
VOCs (8240):		
Benzene	76-127	-
Trichloroethylene	71-120	-
SVOCs (8270):		
Pyrene	26-127	-
Phenol	12-110	-

1. Identification of variable and USEPA analytical method with example volatile and semivolatile organic compounds (VOCs and SVOCs, respectively).
2. Matrix spike (MS) and laboratory control sample (LCS) acceptance criteria in percent recovery. Inorganic criteria from USEPA national functional quidelines. Organic criteria from CLP SOW Forms III VOC-1 and SV-1.

Table 3a. Reported Organic Compounds

	Highest Concentrations[1]	
Category	1996	1997
VOCS:		
Halocarbon	236.	172.
Petroleum Hydrocarbon	29.6	ND
Trihalomethane	26.3	5.08
SVOCS:		
Petroleum Hydrocarbon	44.	ND
Phenolic	175.	ND
Phthalate	72.3	43.2

1. Highest reported concentration of any compound in category out of 19 wells sampled in both years.

Table 3b. Reported Organic Compounds

	Number of Wells Reported In[1]	
Category	1996	1997
VOCS:		
Halocarbon	6.	3.
Petroleum Hydrocarbon	2.	0.
Trihalomethane	12.	1.
SVOCS:		
Petroleum Hydrocarbon	3.	0.
Phenolic	7.	0.
Phthalate	12.	6.

1. Number of wells out of 19 sampled in both years in which any compound in the indicated category was reported at any concentration.

Table 4. Ground/Surface Water Relationship

Variable	Wells[1]	River[2]
Major Ions:		
Chloride	6.96	300.
Sodium	6.76	340.
Sulfate	323	150.
Elements:		
Arsenic	6.85	2.
Barium	725.	130.
Iron	13.2	0.01

1. Site data. Mean for upgradient monitoring wells (1994-1997).
2. USGSdata. Median for river at nearby gaging station (1981-1995),

Table 5. Grouped Inorganic Data[1]

Data Set	Major Cations			
	Ca	Mg	K	Na
1996 Data:				
BF	62.2	4.75	1.04	35.55
UF	59.4	2.97	.5	0.5
BF:UF Ratio	1.04	1.60	2.06	8.46
1997 Data:				
BF	58.66	4.47	.55	3.06
UF	58.48	4.02	.5	2.76
BF:UF Ratio	1.00	1.11	1.1	1.11
Data Set	Major Anions			
	HCO_3	Cl	NO_3	SO_4
1996 Data:				
BF	204.	7.31	12.8	33.5
UF	181.	5.82	6.69	16.6
BF:UF Ratio	1.13	1.26	1.91	2.02
1997 Data:				
BF	177.	3.93	7.62	10.2
UF	174.	4.65	4.52	9.5
BF:UF Ratio	1.02	0.845	1.69	1.07
Data Set	Other Variables			
	Al	Fe	Silica	TDS
1996 Data:				
BF	1.21	0.94	8.72	305.
UF	0.10	0.05	9.68	196.
BF:UF Ratio	12.1	18.8	0.901	1.56
1997 Data:				
BF	0.31	0.10	9.2	231.
UF	0.29	0.06	3.8	226.
BF:UF Ratio	1.06	1.67	2.42	1.02

1. All concentrations are median values for grouped data in units of mg/L.

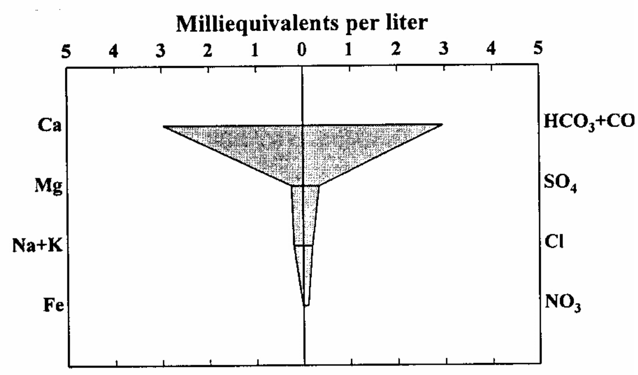
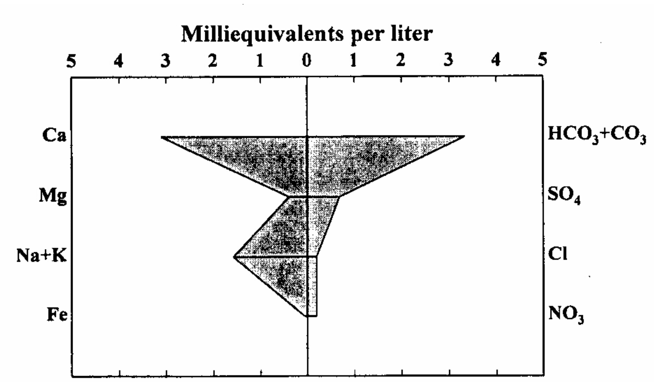


Figure 1. Grouped Median Data STIFF Diagrams - 1996

a. Wells in unfilled boreholes (UF).



b. Wells in bentonite filled boreholes (BF).

GENERAL

SAMPLE INTRODUCTION TECHNIQUES FOR FAST GC ANALYSIS OF ORGANOCHLORINE PESTICIDES

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ABSTRACT

Advances in GC instrumentation in recent years have allowed the analysis of organochlorine pesticides to become more efficient. Pressure programable injectors, for example, have allowed analysts to reduce run times as well as control injector phenomena such as vapor cloud expansion and thermal degradation. GC analysts in environmental laboratories have many options available to them in configuring instrumentation, especially in the techniques they choose for sample introduction. When attempting to maximize the benefits of modem GC instrumentation, analysts must be prepared to adapt their working knowledge of classical GC techniques to newer ones. At the National Air and Radiation Environmental Laboratory (NAREL) we learned that several of our ideas about classical splitless injections had to be modified when we optimized SW846 Method 8081 for speed, Endrin/DDT degradation, and chromatographic resolution.

In an attempt to reduce the run time for SW846 Method 8081, we configured a GC with dual pressure programmable injectors, two dissimilar 0.53 mm capillary columns, and dual ECDs. While the biggest time savings resulted from a relatively high initial oven temperature, having the ability to pressure program the injectors also helped to reduce run times. Programming the injectors at a high initial pressure also reduced Endrin/DDT degradation by insuring a short injector residence time. A high initial oven temperature and high initial injector pressure presented a challenge since high pressure applications typically depend on low initial oven temperatures to achieve solvent focusing. In this analysis solvent focusing is not practical because the boiling point difference between the solvent, hexane, and the earliest elating compound is too large. We found that although we wanted to use techniques that seemed to preclude each other we could empirically match our starting oven temperature with a relatively high initial injector pressure and have a degree of cold trapping to achieve both short GC run times, low Endrin/DDT degradation, and good chromatographic resolution. This deviation from classical splitless injection used both the principles of solvent focusing and high pressure injection to achieve the desired goal. The result was a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation, good resolution on difficult analyte pairs, and all the benefits of splitless injections.

INTRODUCTION

When attempting to maximize the benefits of modern GC instrumentation, analysts must balance their desire to improve the efficiency of an analysis with certain pragmatic concerns: (1) ease of maintenance, (2) use of standard consumables, and (3) ruggedness of new procedures. At the NAREL we wanted a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation, good resolution on difficult analyte pairs, and all the benefits of splitless injections. We also wanted the resulting chromatographic system to be one that was easy to use by any reasonably trained analyst. Most of the modifications employed in our design were in the sample introduction part of the chromatographic analysis.

We configured a GC with dual pressure programmable injectors, two dissimilar 0.53 mm capillary columns, and dual ECDs. Although most of the work was in choosing the appropriate sample introduction techniques, there were other parameters to optimize. For example, we chose a relatively high initial oven temperature to reduce the cycle time of the analysis We also adjusted the detector makeup gas flow to achieve acceptable sensitivity. We wanted to take advantage of injector pressure programming which has become standard equipment on most GCs. We chose splitless injections over direct injections because we believe the splitless technique to be more rugged. In our dual injector system, we kept the injector pressures similar during injection and programmed them differently after the split valve opened to achieve chromatographic resolution. We chose a single taper inlet sleeves because they are easily obtainable and easy to maintain. We chose a compromise initial oven temperature that was hot enough to keep the GC cycle time short and low enough to prevent the earliest eluting compounds from tailing too much. This is different from classical splitless injection technique where the initial oven temperature is kept low until most of the sample can slowly migrate from the inlet sleeve to the head of the column. This deviation from classical splitless injection used both the principles of solvent focusing and high pressure injection to achieve the desired goal. The result was a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation, good resolution on difficult analyte pairs, and all the benefits of splitless injections.

EXPERIMENTAL

A mix containing twenty pesticides, two surrogate standards, and three internal standards (Ultra Scientific) was prepared from the dilution of certified standard mixes with pesticide grade hexane (Burdick & Jackson). Our experimental results are best discussed in terms of injection technique, pressure programming, and column selection.

We decided to use splitless injections rather than direct injections to both simplify routine maintenance and increase system ruggedness. Using a 4 mm ID single taper inlet liner eased routine column maintenance because the insertion distance of the column into the liner was the only critical step. A 1.0 µL volume of hexane extract will expand to approximately 300 µL of vapor at 6.5 psig. This is easily contained within the 900 µL of available volume in a 4mm ID liner. We found that a pressure increase after injection provided two benefits: (1) the vapor cloud moved onto the analytical column in a smaller plug and (2) the compounds were pushed through the column quicker. We chose 12.4 psig as the injector pressure which resulted in a column linear velocity of 102 cm/sec. We used 120ºC as our initial oven temperature. These represent a compromise between classical solvent focusing and high pressure injection. Moving the sample vapor cloud onto the column quickly has several benefits. Along with keeping early eluting peaks from tailing, high pressure injections dramatically reduce Endrin/DDT degradation. Combined Endrin/DDT degradation rarely exceeds 5.0% with this configuration. Optimization of the opening and closing times for the split vent are still crucial for quantitative accuracy.

We chose analytical columns based on chromatographic separation and ruggedness. A 5% diphenyl 95% dimethyl polysiloxane column such as Restek's Rtx-5, provided both the good chromatographic separation and a high temperature limit. As a confirmation column we chose a hybrid column developed by Tammy Carey[1] that met our chromatographic needs. The GC oven temperature program is given in Table 1 along with the other chromatographic conditions. The temperature program was optimized to separate critical pairs such as Endosulfan I/alpha Chlordane and Dieldrin/DDE on the Rtx-5 column and Heptachlor epoxide/gamma-Chlordane and Endosulfan II/DDT on the Hybrid column. Chromatograms of the twenty-two organochlorine pesticides are shown in Figure 1 and calibration curve summaries are given in Tables 2 and 3.

Table 1. Chromatographic Conditions

GC Parameter	Value
Carrier Gas	Helium
Injector	Splitless, 1µL, Purge Delay 0.75 min. Inlet Temperature 250ºC
Pressure Program	Initial Linear Velocity: 102 cm/sec. @ 120ºC Rtx-5 12.4 psi Hold 0.50 min. to 5.8 psi @ 99.0 psi/min. Hold 4.00 min. to 14.5 psi @ 0.75 psi/min. to 19.0 psi @ 1.5 psi/min. Hybrid 12.4 psi Hold 0.50 min. to 7.5 psi @ 99.0 psi/min. Hold 6.00 min. to 14.0 psi @ 0.75 psi/min. to 20.0 psi @ 1.5 psi/min.
Temperature Program	120ºC Hold 0.5 min. to 150ºC @ 30ºC/min. to 200ºC @ 4ºC/min. to 285ºC @ 20ºC/min. Hold 1.0 min.
Detector	N_2 Makeup @ 50 mL/min. Anode Purge @ 5mL/min. ECD @ 310ºC

SUMMARY

At the NAREL we wanted a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation, good resolution on difficult analyte pairs, and all the benefits of splitless injections. We also wanted the resulting chromatographic system to be one that was easy to use by any trained analyst. Although most of the work was in choosing the appropriate sample introduction techniques, there were other parameters to optimize. We deviated from classical splitless injection technique slightly to accommodate the use of pressure programmable injectors. This deviation from classical splitless injection used both the principles of solvent focusing and high pressure injection to achieve the desired goal. The result was a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 20 minutes, very low Endrin/DDT degradation, good resolution on difficult analyte pairs, and all the benefits of splitless injections.

REFERENCES

1. Carey, Tamela; *Chlorinated Pesticide Analysis Using Hybrid Columns* (unpublished), CH2M Hill, Montgomery, AL

Table 2. Calibration Curve Summary of 5% Diphenyl Column

INITIAL CALIBRATION REPORT

INSTRUMENT: GC#5/FRONT (5%DP)
CALIBRATION DATE: 03/09/97
METHOD: SW846/ 8081
SEQUENCE: E030997A
DATA FILES: 010F010 - 014F0101

COMPONENT	5ppb	10ppb	25ppb	50ppb	100ppb	SD	MEAN RRF	%RSD	P/F
Pentachlorobenzene/IS#1	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Tetrachloro-m-xylene	0.65	0.66	0.72	0.74	0.73	0.04	0.70	5.13	
alpha-BHC	0.51	0.54	0.63	0.75	0.80	0.11	0.65	17.61	
beta-BHC	0.37	0.37	0.39	0.40	0.39	0.01	0.38	3.40	
Lindane	0.50	0.53	0.60	0.69	0.74	0.09	0.61	14.88	
delta-BHC	0.46	0.47	0.54	0.65	0.69	0.09	0.56	16.77	
Heptachlor	0.70	0.67	0.68	0.67	0.66	0.01	0.68	1.99	
Aldrin	1.16	1.28	1.37	1.40	1.40	0.09	1.32	7.05	
Heptachlor Epoxide	1.47	1.46	1.46	1.43	1.35	0.04	1.43	2.94	
gamma-Chlordane	1.65	1.65	1.70	1.70	1.61	0.03	1.66	2.09	
Endosulfan I	1.35	1.37	1.42	1.41	1.34	0.03	1.38	2.29	
alpha-Chlordane	1.69	1.71	1.78	1.77	1.67	0.04	1.73	2.60	
Dieldrin	1.35	1.29	1.31	1.32	1.25	0.03	1.31	2.65	
DDE	1.44	1.35	1.47	1.59	1.55	0.08	1.48	5.62	
o-p'-DDD/IS#2	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Endrin	1.46	1.40	1.37	1.37	1.28	0.06	1.37	4.26	
Endosulfan II	1.40	1.48	1.53	1.50	1.38	0.06	1.46	4.01	
DDD	1.12	1.05	1.02	1.07	1.01	0.04	1.05	3.60	
Endrin Aldehyde	1.16	1.17	1.18	1.10	1.01	0.07	1.12	5.79	
Endosulfan Sulfate	1.33	1.22	1.17	1.17	1.13	0.07	1.20	5.93	
DDT	1.22	1.12	1.15	1.19	1.17	0.04	1.17	3.05	
Endrin Ketone	1.55	1.51	1.51	1.50	1.43	0.04	1.50	2.56	
Methoxyclor	0.45	0.46	0.45	0.45	0.43	0.01	0.45	2.36	
Pentabromobiphenyl/IS#3	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Decachlorobiphenyl	1.55	1.53	1.44	1.35	1.34	0.09	1.44	6.16	

COMMENTS:

Table 3. Calibration Curve Summary of Hybrid Column

INITIAL CALIBRATION REPORT

INSTRUMENT: GC#5/REAR (HYBD)
CALIBRATION DATE: 03/09/97
METHOD: SW846/ 8081
SEQUENCE: E030997A
DATA FILES: 060R010 - 064R0101

COMPONENT	5ppb	10ppb	25ppb	50ppb	100ppb	SD	MEAN RRF	%RSD	P/F
Pentachlorobenzene/IS# 1	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Tetrachloro-m-xylene	0.76	0.79	0.89	0.80	0.81	0.04	0.81	5.47	
alpha-BHC	0.65	0.65	0.77	0.82	0.94	0.11	0.77	14.20	
Lindane	0.63	0.64	0.75	0.79	0.89	0.10	0.74	13.15	
beta-BHC	0.46	0.39	0.42	0.42	0.47	0.03	0.43	6.62	
Heptachlor	0.95	0.94	0.93	0.90	0.87	0.03	0.92	3.35	
delta-BHC	0.54	0.55	0.63	0.70	0.81	0.10	0.65	15.67	
Aldrin	0.64	0.63	0.68	0.70	0.78	0.05	0.69	7.89	
Heptachlor Epoxide	1.10	1.10	1.12	1.07	1.12	0.02	1.10	1.88	
gamma-Chlordane	1.29	1.44	1.47	1.43	1.50	0.07	1.42	5.17	
alpha-Chlordane	1.30	1.48	1.46	1.39	1.40	0.06	1.40	4.49	
DDE	1.29	1.28	1.29	1.28	1.38	0.04	1.30	2.86	
Endosulfan I	1.35	1.25	1.25	1.20	1.25	0.05	1.26	3.99	
o-p'-DDD/IS#2	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Dieldrin	1.22	1.15	1.19	1.22	1.23	0.03	1.20	2.46	
Endrin	1.15	1.12	1.16	1.12	1.15	0.02	1.14	1.48	
DDD	0.91	0.85	0.87	0.92	0.92	0.03	0.90	3.06	
Endosulfan II	1.06	1.03	1.08	1.07	1.05	0.02	1.06	1.59	
DDT	1.11	1.03	1.04	1.04	1.06	0.03	1.06	2.55	
Pentabromobiphenyl/IS# 3	1.00	1.00	1.00	1.00	1.00	0.00	1.00	NA	NA
Endrin Aldehyde	1.09	1.04	1.01	0.93	0.89	0.07	0.99	7.18	
Methyoxyclor	0.61	0.58	0.55	0.51	0.48	0.05	0.55	8.51	
Endosulfan Sulfate	1.40	1.36	1.41	1.23	1.22	0.08	1.32	6.25	
Endrin Ketone	1.80	1.73	1.70	1.63	1.55	0.06	1.63	3.77	
DCB	1.73	1.80	1.82	1.69	1.54	0.10	1.71	5.84	

COMMENTS:

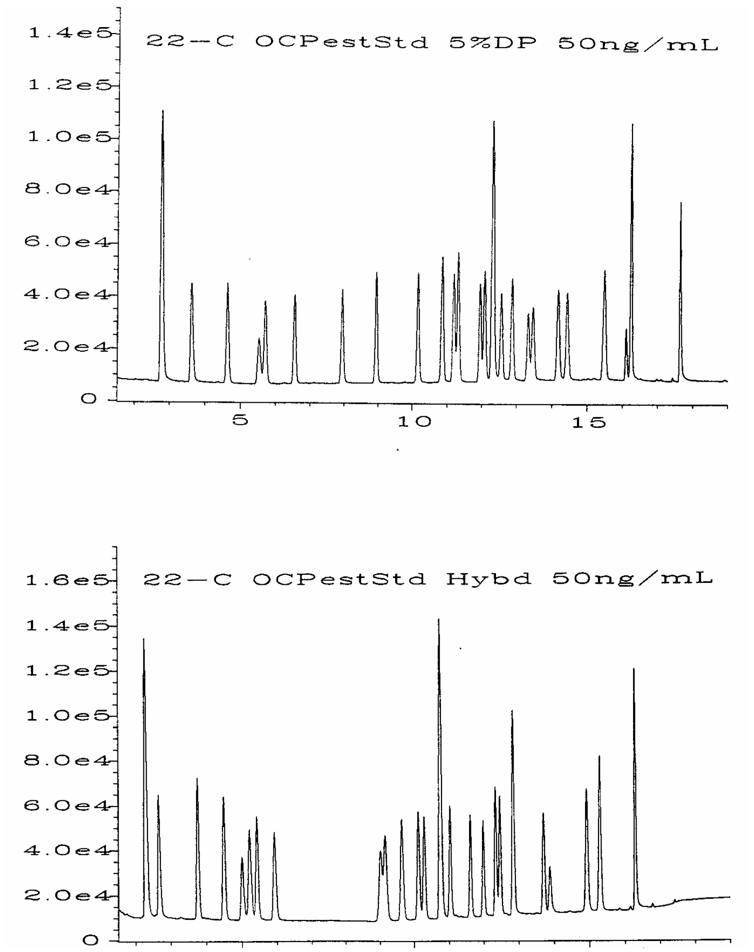

Figure 1. Chromatograms of twenty-two Organochlorine Pesticides on a dueal injector GC system.

IONSPRAY LC/MS METHOD FOR THE QUANTITATION OF MAJOR DEGRADATION PRODUCTS OF BENOMYL

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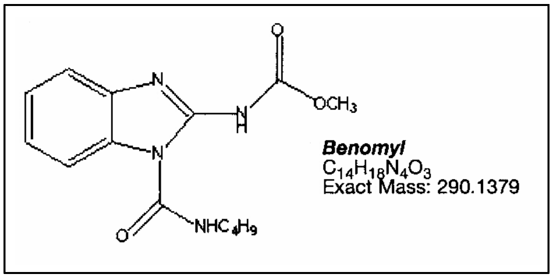
OVERVIEW

An existing High Performance Liquid Chromatography (HPLC) UV quantitative method has been directly transferred to an ionspray single quadrupole LC/MS assay resulting in an immediate gain in sensitivity and selectivity. This ionspray method was then modified for narrow bore HPLC, obviating the need to split while reducing the analysis time and improving the limit of quantitation. The narrow bore HPLC method was linear over three orders of magnitude with increased robustness and case of use.



Benomyl
$C_{14}H_{18}N_4O_3$
Exact Mass: 290.1379

INTRODUCTION

The determination and quantification of polar pesticides and their degradation products in environmental analytical chemistry is gaining importance because of their persistence and toxicity. Furthermore, many countries have now passed legislation to ensure that pesticides are used safely and responsibly in order to protect the public from unsafe levels of pesticide residues. Due to the high polarity, low volatility and thermolability of carbamates, GC and GC/MS methods are not amenable to this class of compounds. HPLC with UV detection has been the standard analytical method for analysis and quantitation of polar compounds. Benomyl, a carbamate and a widely used systemic fungicide for disease control in crops, poses additional analytical challenges to the environmental chemist due to its extreme instability in the environment. Benomyl decomposes to three stable major degradation products: 2-aminobenzimidazole (2-AB), methyl 1-H-benzimidazol-2-ylcarbamate (MBC), and 3-butyl-2,4-dioxo-s-triazino [1,2-a] benzimidazole (STB).

EPA Method 631 for the determination of benomyl and MBC in industrial and municipal wastewater restricts the detection and quantitation to MBC only since benomyl is hydrolyzed to MBC in this method. This isocratic UV method has a Method Detection Limit (MDL) of 8.7 ppb for MBC.

The UV method adapted in this report monitors the three major degradation products of benomyl by gradient elution. The UV analysis has a method detection limit of 2 ppb for 2-AB, MBC, and STB.

METHOD

Materials

2-AB was obtained from Aldrich Chemical Company (Milwaukee, WI). MBC was obtained from Chem Services (West Chester, PA) and STB was obtained from E.I. du Pont Nemours & Co. (Wilmington, DE). Solvents used for HPLC and extraction were HPLC grade acetonitrile, methanol and water from JT Baker (Philipsburg, NJ). The formic acid used in the HPLC solvents, as well as the injection solvent, was from Sigma (St. Louis, MO). The standard bore (4.6 x 250 mm) HPLC column was a C18 with a 5-µm particle size by Whatman (Clifton, NJ). The narrow bore column (2 x 50 mm) was a Monitor C18 with a 3-µm particle size by Column Engineering (Ontario, CA). A Waters Oasis (Milford, MA) 3-mL, 60-mg SPE cartridge was used for the solid phase extraction.

Preparation. Benlate Extraction Procedure

A Benlate mix spike solution was comprised of a mixture of 2-AB and STB in methanol at a concentration of 2 ppm. 200 mL of water sample was poured into a 400-mL beaker. HPLC grade water was used for blanks and laboratory fortified blanks. The pH of all samples was checked and recorded using a pH meter. For any spiked samples (laboratory fortified blanks and matrix spikes), 200 µL of Benlate mix spike solution was added and mixed well. Two Normal NaOH was added to adjust the pH of all the samples to 10. The solid phase extraction (SPE) cartridge was conditioned by aspirating 5 mL of methanol through the cartridge followed by 10 mL of HPLC grade water without allowing the cartridge to dry. The sample was filtered through the conditioned SPE cartridge under vacuum. The sample beaker was then rinsed with 5 mL of HPLC grade water adjusted to pH 10. The rinse was passed through the SPE cartridge and vacuum dried for 3 min. Elution with 5 mL of methanol and collection of the eluate into a 15 mL centrifuge test tube was completed. The eluate was dried down with nitrogen in a water bath at 40ºC to a volume of 1 mL. One mL of 0.2% formic acid was added and mixed well.

HPLC Conditions

A Shimadzu VP series HPLC (Columbia, MD) was used with the gradients, flow rates and columns listed in Table 1.0 and Table 1.1. The flow from the standard bore column was split down from 1 mL/min to approximately 200 µL/min into the Turbolonspray source at ambient temperature. For the narrow bore column no split was necessary and the entire effluent was sent into a Turbolonspray source set to 200ºC.

Table 1.0. HPLC Gradient

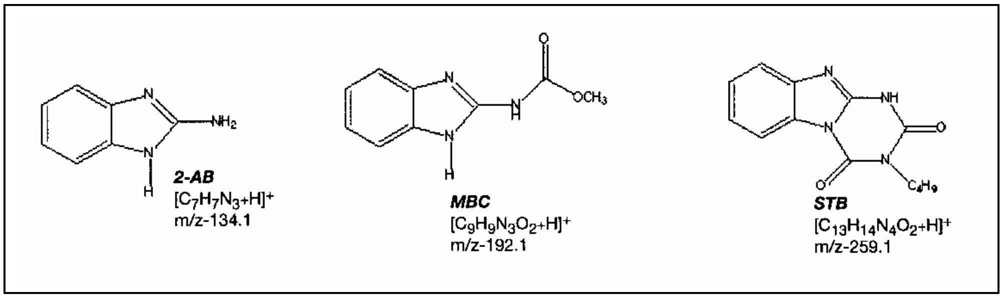
Standard Bore Column		**Solvent A**	**Solvent B**
4.6 x 250 mm	Time (min)	0.1% Formic Acid	Methanol + 0.1% Formic Acid
Flow rate: 1 mL/min	0	70	30
Whatman C18 5 µm	10	30	70
	20	15	85
	20.1	70	30
	30	70	30

Table 1.1. HPLC Gradient

Narrow Bore Column	Time(min)	0.1% Formic Acid	Acetonitrile + 0.1% Formic Acid
2 x 50 mm	0	100	0
Flow rate: 0.2 mL/min	0.85	50	50
Column Engineering	2.25	45	55
Monitor C18 3 µm	4	45	55
	6	30	70
	7	30	70
	7.1	100	0
	10	100	0

Mass Spectrometer

A PE Sciex API 150 (Concord, Ontario, Canada) single quadrupole mass spectrometer was operated in positive ion mode with a Turbolonspray source. The source temperature was ambient for the standard bore HPLC column and was set to 200ºC for the narrow bore column. The compounds were monitored using selected ion monitoring (SIM) with the following m/z values:



2-AB
$[C_7H_7N_3+H]^+$
m/z-134.1

MBC
$[C_9H_9N_3O_2+H]^+$
m/z-192.1

STB
$[C_{13}H_{14}N_4O_2+H]^+$
m/z-259.1

The ion optics path was optimized for each compound separately in the separations solvent. The values for the orifice, ring and Q0 are listed in Table 2.0. The mass spectrometer was operated at unit resolution with an ionspray voltage of 4600 V.

Table 2.0. Ion Path Voltages

Compound	OR	RNG	Q0
2-AB	45	160	-4
MBC	20	120	-3
ST13	30	155	-4

RESULTS

Initially the primary emphasis was on transferring an already validated UV HPLC method to a single quadrupole MS method altering as few parameters as possible. Only two changes to the original procedure were necessary for the method transfer. Formic acid was added to the mobile phase of the HPLC solvents, and the injection solvent was changed to contain a final concentration of 0.1% formic acid in 50% methanol. All other parameters remained the same. As a consequence of the change in pH, the elution order of the compounds changed but chromatographic resolution was maintained and all compounds were baseline resolved. The eluant from the 4.6-mm column was initially split to 50 µL/min into the Turbolonspray source at room temperature. Occasionally at a high percentage of organic, the 50-µL/min split into the mass spectrometer would lose flow resulting in a loss of signal. This was corrected by decreasing the split ratio sending approximately 200 µL/min into the ion source at the expense of sensitivity. Nevertheless, the limit of quantitation for the standards (0.01 ppm) was an order of magnitude better than that of the UV analysis of standards (0.1 ppm). (See Figure 1.0 and Figure 1.1.)

The Method Detection Limit (MDL) was calculated with the following equation:

$$\text{MDLcalculated} = t \times s \times V_{ext}/V_{sample}$$

V_{ext} = 2 mL t = Student Coefficient
V_{sample} = 200mL s = Standard Deviation

Table 3.0 contains the solid phase extraction validation data and Table 4.0 contains the MDL calculations for both UV and LC/MS analyses. While the calculated MDL for the UV and LC/MS methods are similar, the actual MDL achieved by the two methods is an order of magnitude different.

Table 3.0. SPE Validation for Water

Recoveries																	
UV 4.6 x 250 mm		**MDL-1**		**MDL-2**		**MDL-3**		**MDL-4**		**MDL-5**		**MDL-6**		**MDL-7**			
Compound	Spike Level	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L	%	%Mean	SD	%RSD
2-AB	5 µg/L	2.5	50	2.5	50	2.7	54	2.7	54	3.2	64	3.3	66	3.1	62	57.1	6.7	12
MBC	5 µg/L	5	100	5.3	106	5.4	108	4.6	92	56	112	5.3	106	5.2	104	104	6.4	6
STB	5 µg/L	5.4	108	5.5	110	5.8	112	4.7	94	5.7	114	5.5	110	5.3	106	108	6.6	6
LC/MS 4.6. 250 mm																		
2-AB	2 µg/L	1.74	87	1.86	93	1.76	88	1.9	95	1.86	93	1.94	97	1.64	82	90.7	3.9	4
MBC	2 µg/L	1.98	99	2.12	106	2.04	102	2.2	110	2.18	109	2.26	113	2.18	109	107	5.2	5
STB	2 µg/L	1.57	79	1.64	82	1.54	77	1.58	79	1.54	77	1.62	81	1.66	83	79.7	2	3

Table 4.0. MDL

Method Detection Limit					
UV 4.6 x 250mm					
Compound	Student Coefficient	n	Std. Deviation	MDL (calculated)	MDL (actual)
2-AB	3.143	7	6.7	0.21 ppb	2 ppb
MBC	3.143	7	6.4	0.20 ppb	2 ppb
STB	3.143	7	6.6	0.21 ppb	2 ppb
LC/MS 4.6. 250 mm					
2-AB	3.143	7	3.9	0. 12 ppb	0.2 ppb
MBC	3.143	7	5.2	0.16 ppb	0.2 ppb
STB	3.143	7	2	0.063 ppb	0.2 ppb

In order to improve the setup and ease of use the LC/MS method was altered further. A 2 X 50-mm HPLC column replaced the larger diameter column and the entire eluant flow was sent directly into the Turbolonspray source. The source was operated at 200ºC. This source temperature gave the best overall response for the three compounds of interest while not significantly adding to the background signal of the final method. The initial gradient was based on the same column volumes and used the same buffer system of the larger column. The result was a fine separation of 2-AB and MBC but STB did not elute as a sharp peak. With the addition of heat the methanol solvent system generated an additional problem. The background signal increased dramatically making detection of the low standards difficult. All efforts to reduce the background with methanol as the organic solvent failed. Methanol was replaced with acetonitrile, resulting in much lower background counts and a much improved STB peak shape. The gradient was changed to accommodate the stronger solvent. In fact, the peak shapes improved for all three analytes. 2-AB and MBC each elute in roughly 20 µL and are baseline-resolved. STB elutes in approximately 100 µL. Because of this difference in elution volumes a period MS method generated better S/N for each compound. This reduced elution volume from the narrow bore column improved the limit of quantitation (LOQ) even further. While the reduction in column dimension should only result in a four-fold gain in sensitivity, the above changes resulted in a 50-fold gain since only 10 µL were injected onto the 2-mm column versus 100 µL injected onto the 4.6-mm column. The small volume of the 2-mm column as compared to the standard bore column also reduced the analysis time from 30 minutes to 10 minutes.

Figures 1.0, 1.1 and 1.2 are views of the low standards for each method. Each has a S/N greater than 10:1. The LOQ for the standards is 0.1 ppm, 0.01 ppm, and 0.002 ppm for the UV, 4.6, and 2-mm methods, respectively. The resultant calibration curves are shown in Figure 2.0. A linear 1/X weighting was used for the LC/MS analyses while no weighting was used in the UV analysis. Table 5.0 lists the percent deviation of the mean from the theoretical (%DMT) and the %RSD obtained over five days for the various levels using the 2-mm LC/MS method. Table 5.0 demonstrates the high degree of accuracy and consistency required for successful quantitative results.

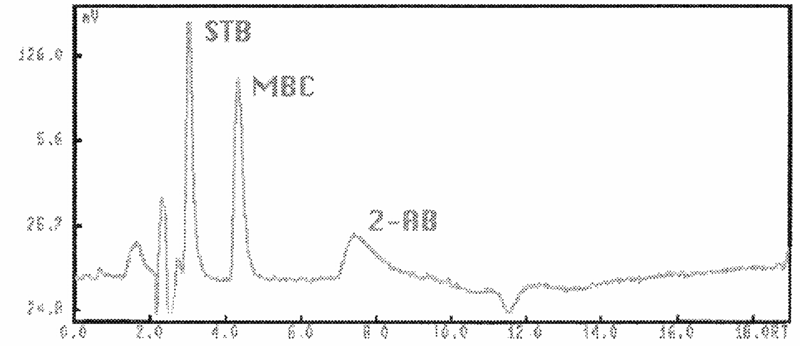


Figure 1.0. UV Low Standard (0.1 ppm; 100-µL injection volume).

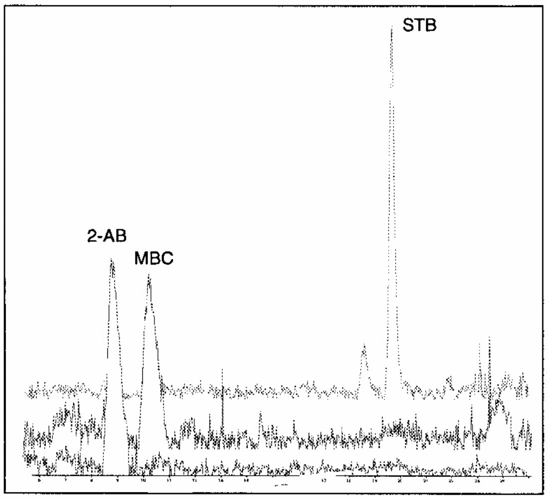


Figure 1.1. 4.6 x 250 mrn Low Standard (0.01 ppm; 100-µL injection volume).

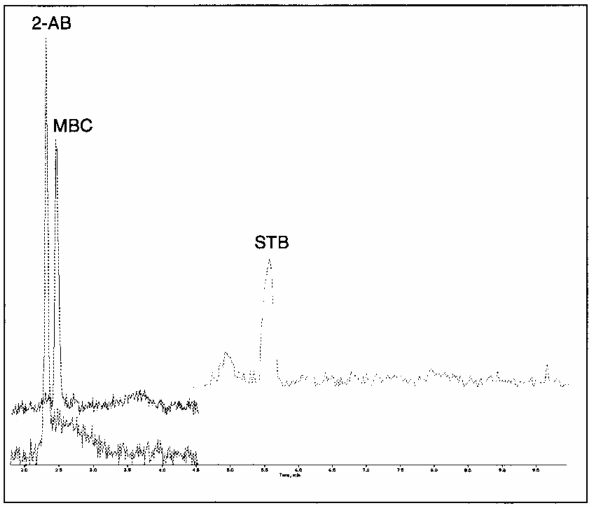


Figure 1.2. 2 x 50 mm Low Standard (0.002 ppm; 10-µL injection volume).

Table 5.0. %DMT Statistics

Five-Day Percent Deviation from Theoretical LC/MS 2 x 50 mm method						
	2-AB		MBC		STB	
Level	%DMT	% RSD	%DMT	% RSD	%DMT	% RSD
	2-AB	2-AB	MBC	MBC	STB	STB
1000 ppb	96.19	1.12	97.8	0.44	99.45	0.05
200 ppb	111.15	0.94	107.69	1.87	105.99	1.38
100 ppb	110.49	2.35	106.79	1.98	105.38	2.06
20 ppb	106.65	1.95	102.2	2.81	98.76	5.81
10 ppb	104.38	4.04	99.57	2.38	91.64	5.67
2 ppb	94.05	2.51	98.91	4.67	108.2	11.72
1 ppb	78.97	13.26	95.67	9.29	114.25	16.74

While the 0.001-ppm standard is detected with the 2-mm method, the %RSD for the accuracy of the three compounds was deemed to be too high for the LOQ. The MDL-7 for the 2 x 50-mm LC/MS method needs to be completed, but based on the previous results for the standards the MDL should be approximately 0.02 ppb.

CONCLUSIONS

A method was developed to quantitate the major degradation products of benomyl in a simple, single quadrupole LC/MS assay. An existing UV HPLC method was slightly modified for analysis by a PE Sciex. API 150 mass spectrometer. An immediate order of magnitude gain in sensitivity over the UV MDL resulted. This LC/MS method obviates the additional step of hydrolysis described in EPA Method 631, allowing for direct quantitation of the major degradation products of benomyl. Currently the benomyl LC/MS method can be used with extraction protocols for water. Additional optimization of the HPLC and MS method produced further gains in sensitivity and also simplified the system setup. The narrow bore method requires the validation process to be completed, but this should not prove difficult based on the clean matrix provided by the SPE protocol and the consistency of the standards analyzed. The increased specificity afforded by MS also allowed for a reduction in HPLC and data analysis time.

Future work will result in the development of extraction protocols for waste and sediment. Also, implementation of an internal standard should improve the results obtained by this method.

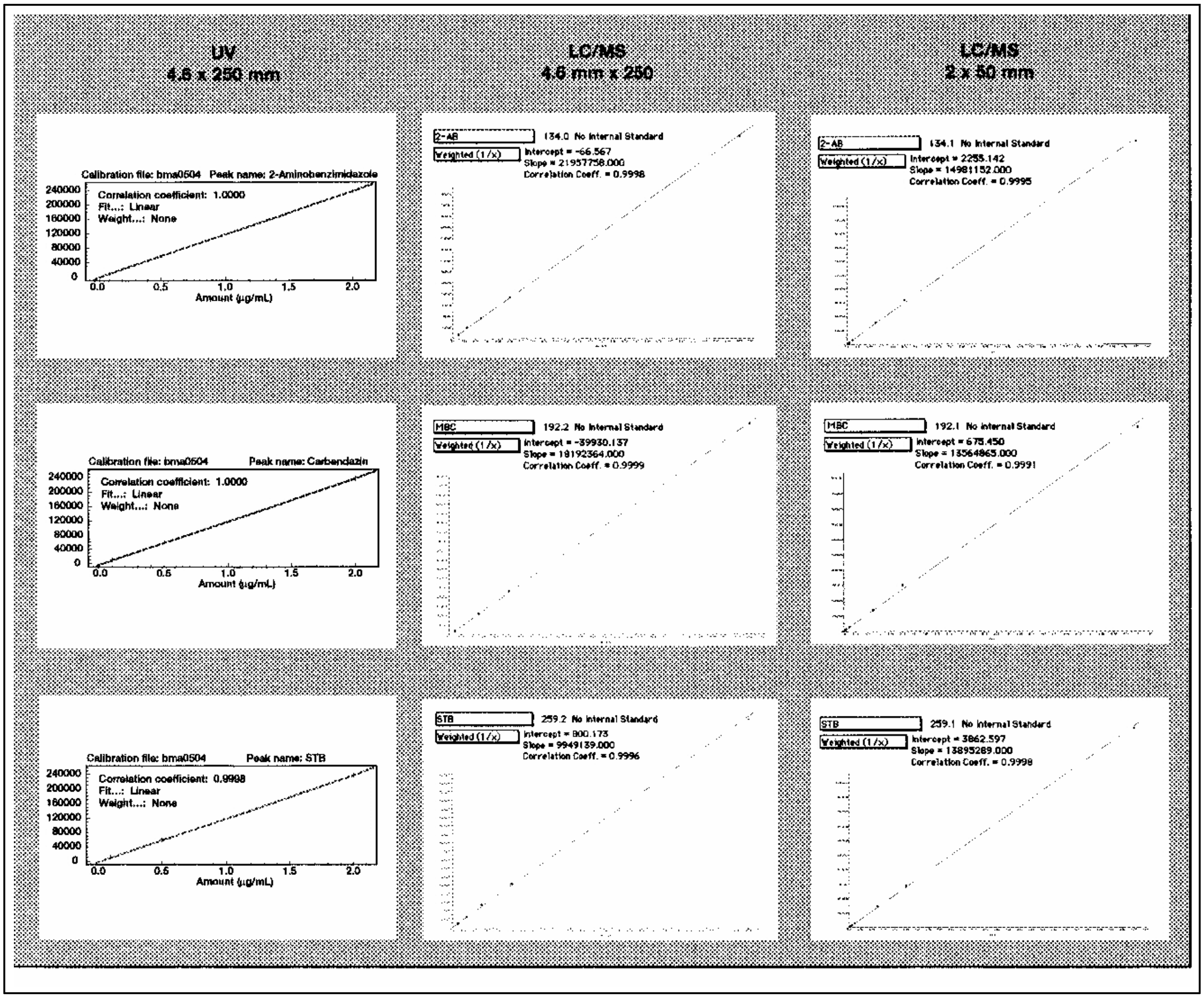


Figure 2.0. Calibration Curves for 2-AB, MBC, and STB.

METHODS OPTIMIZATION OF MICROWAVE ASSISTED SOLVENT EXTRACTION TECHNIQUES FOR VARIOUS REGULATORY COMPOUNDS

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We have seen a period of rapid growth in the separation sciences, with gas and liquid chromatography as well as the hyphenated techniques becoming commonplace. There is a need to streamline the extraction techniques preceding these chromatographic analyses. Time and solvent usage have become critical factors. In response to this need several new sample preparation technologies have emerged. As a result analysts are faced with the challenge of adapting current methods or developing entirely new ones depending on the extraction technology they use.

Microwave Assisted Solvent Extraction is a new technique that works with existing solvent regimes with minimal modifications and significant solvent reduction. It also has the benefit of reducing the extraction time. This study will review the methods optimization process when using a closed vessel microwave assisted solvent extraction technique. It will focus on extraction temperature, sample water content and ratios for solvent mixtures. Recovery data will be presented for pesticides and fungicides from reference soils and vegetable samples.

NEW DEVELOPMENTS IN CLOSED VESSEL MICROWAVE DIGESTION TECHNOLOGY FOR PREPARATION OF DIFFICULT ORGANIC SAMPLES FOR AA/ICP ANALYSIS

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Microwave digestion techniques are well accepted as a means of preparing samples prior to AA and ICP analysis. Pressurization of the sample vessel accelerates the dissolution process by permitting acids to attain higher temperatures than under ambient conditions. However, it has been historically difficult to control the microwave digestion process under ultra-high temperature and pressure conditions. As well, throughput of difficult high-pressure samples using conventional microwave instrument technology has been limited, thus inhibiting its use for preparation of some difficult organic and inorganic samples. This paper will demonstrate new microwave instrument technology for optimization of ultra-high pressure and temperature conditions for microwave preparation of difficult organic and inorganic samples for AA and ICP analysis. Data will be provided to demonstrate the digestion performance under significantly elevated pressure and temperature conditions as well as the impact of such conditions on the microwave preparation instrumentation.

EVALUATION OF ICP-OES AND ICP-MS FOR ANALYSIS OF THE FULL TCLP INORGANIC TARGET ANALYTE LIST

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Abstract

Toxicity Characteristic testing is performed to assess the potential of a material to leach hazardous constituents after disposal in a landfill. The Toxicity Characteristic Leaching Procedure (TCLP) extract solution is analyzed for 31 organic components and 8 metals and if the regulated limits are exceeded (Table 1) the material is considered hazardous and must be treated appropriately.

Currently, ICP-OES and ICP-MS have the technical capability of determining the full suite of TCLP elements in one run. EPA ICP-OES method 6010B includes Hg in the target analyte list. EPA ICP-MS draft method 6020A now includes Se and Hg in the target analyte list. This provides an opportunity to demonstrate the utility of TCLP analysis using one sample preparation and one technique for analysis.

Compliance with the generally accepted requirements of the RCRA program will be demonstrated for the full suite of TCLP analytes including mercury. ICP-OES and ICP-MS will be compared for the analysis.

The results will be validated with the analysis of the required Quality Control for performance-based methods and will include detection limits, spike recoveries, and duplicate sample analytical data.

Experimental

Raw TCLP extracts were provided by Trinity River Authority in Dallas Texas. They were prepared by digestion with EPA method 3015 using the Multiwave Microwave Digestion System (Perkin-Elmer Corp.). To evaluate the recovery vs. hotplate digestion, for mercury, the samples were also spiked with mercury and digested on a hotplate using method 3020. Gold was added to some samples to evaluate the effect on retention of mercury during the digestion process and resulted in a concentration of 2 mg/L in the final solution.

The samples were analyzed using ICP-OES and ICP-MS, for comparison. The instrumental conditions are shown in Tables 2 and 3.

Table 1. TCLP Metal Limits

Element	**MCL(mg/L)**
As	5.0
Ba	100.0
Cd	1.0
Cr (Total)	5.0
Pb	5.0
Hg	0.2
Se	1.0

Table 2. ICP-OES Instrumental Conditions
Optima 3000 DV

Parameter	**Settings**
RF Power	1500 watts
Nebulizer Flow	0.4 L/min
Auxiliary Flow	0.5 L/min
Plasma Flow	15.0 L/min
Sample Pump Flow	1.5 mL/min
Plasma Viewing	Axial
Processing Mode	Area
Auto integration	5 sec min-20 sec max
Read Delay	45 sec
Rinse	45 sec
Replicates	2
Background Correction	one or two points

Table 3. ICP-MS Instrumental Conditions
ELAN 6000

Parameter	Settings
RF Power	1500 watts
Nebulizer Flow	0.94 L/min
Auxiliary Flow	1.0 L/min
Plasma Flow	15.0 L/min
Sample Pump Flow	1.5 mL/min
Sample/Skimmer Cones	Nickel
Scanning Mode	Peak Hopping
Lens	Lens Scan Enabled
Read Delay	10 sec
Rinse	35 sec
Replicates	3
Detector Mode	Dual Mode

Results and Discussion

The instruments were qualified by measuring method detection limits using the procedures specified in the Federal Register, part 136[1]. The method detection limits are shown in Table 4 and compared with the MCL (shown here in µg/L for easier comparison) for the element. It is generally accepted that the MDL should be ten times less than the MCL to ensure sufficient confidence at the decision-making point. The detection limits for both the ICP-OES and ICP-MS are well below the limits set by the criteria specified.

Table 4. Method Detection Limits

Element	MCL (µg/L)	MDL (µg/L) ICP-OES	MDL (µg/L) ICP-MS
Ag	5000	6	0.007
As	5000	2	0.09
Ba	100,000	0.3	0.01
Cd	1000	0.1	0.03
Cr	5000	0.6	0.05
Hg	200	8	0.34
Pb	5000	2	0.006
Se	1000	3	0.18

The results were measured on the samples digested with the microwave procedure for the full suite of elements. The results are shown in Table 5 and compared with results reported by the supplier. The digested samples compared well with the results provided. The ICP-OES and ICP-MS results compared well with each other, The results were all well below the maximum contaminant levels for all elements.

Table 5. Comparison of Sample Results

Element	ICP-OES Sample 1 (µg/L)	ICP-MS Sample 1 (µg/L)	TR-1 (µg/L)	ICP-OES Sample 2 (µg/L)	ICP-MS Sample 2 (µg/L)	TR-2 (µg/L)
Ag	8	0.1	< 2	6	0.05	<2
As	8	5	<5	6	3.4	<2
Ba	253	214	232	260	218	278
Cd	2	0.4	< 8	1	0.08	< 8
Cr	15	12	11	6	7	5
Hg	< 8	< 0.3	< 0.5	<8	< 0.3	< 0.5
Pb	7	4	4	5	2	< 4
Se	5	4	< 5	2	2	< 5

Predigestion spike recoveries were evaluated for samples digested with the microwave procedure. The samples were spiked with 2.5 mg/L of As, Cr, Pb, Ag, 0. 5 mg/L of Cd, Se, 0.1 mg/L Hg, and 50 mg/L of Ba. The samples labeled "Spike 2" also had gold added (2 mg/L). The spike recoveries are shown in Table 6 for ICP-OES analysis and Table 7 for ICP-MS analysis.

Table 6. ICP-OES Spike Recoveries

Element	Sample 1 Spike 1 %Rec	Sample 1 Spike 2 %Rec	Sample 2 Spike 1 %Rec	Sample 2 Spike 2 %Rec	Blank Spike 1 %Rec	Blank Spike 2 %Rec
Ag	33	2	30	2	63	2
As	104	107	107	108	99	100
Ba	102	102	102	101	101	101
Cd	106	108	107	108	105	106
Cr	100	101	100	101	99	99
Hg	60	62	62	63	54	60
Pb	99	102	100	100	102	103
Se	104	107	105	106	96	96

The spike recoveries were excellent. The silver recoveries diminished with time, as is typical with a nitric-only digestion. Since the ICP-MS analysis was performed first and the ICP-OES analysis was performed after several days had passed the effect is more evident in the ICP-OES results. The addition of small amounts of chloride with the gold solution in the second spike accelerated the precipitation of silver. The mercury spike recoveries were less than expected and may be due to insufficient cooling of the vessels before the solution was transferred. The solutions were not stored in Teflon® bottles, providing another possible source of loss. Since the addition of gold improved the recoveries of mercury only slightly in the microwave digestion, better overall performance may be obtained if the gold is left out. The effect of gold addition on the retention of mercury in a traditional hotplate digestion was investigated. The recoveries compared to spikes digested with microwave are shown in Table 8.

Table 7. ICP-MS Spike Recoveries

Element	Sample 1 Spike 1	Sample 1 Spike 2	Sample 2 Spike 1	Sample 2 Spike 2	Blank Spike 1	Blank Spike 2
Ag	92	6	97	4	106	7
As	104	100	102	104	93	102
Ba	115	120	116	118	117	116
Cd	101	103	103	103	104	103
Cr	96	96	96	99	100	101
Hg	62	53	92	53	55	54
Pb	109	107	109	106	109	106
Se	103	108	98	107	103	113

Table 8. Effect of Gold on Mercury Spike Recovery

	Sample 1 Spike (% Rec)	Sample 1 Spike Dup. (% Rec)	Sample 1 Spike+Gold (% Rec)	Sample 1 Spike Dup. +Gold (% Rec)
Hot Plate Digestion				
ICP-OES	52.1	32.8	56.9	61.5
ICP-MS	44.4	37.0	51.2	47.5
Microwave Digestion				
ICP-OES	60	62	62	63
ICP-MS	62	62	53	53

The addition of gold only slightly improves the recoveries of mercury using the microwave digestion. The hotplate digestion results show more dramatic recovery improvements. In addition, the duplicates are much more consistent in the hotplate digestion when gold is added before the digestion process.

Summary

Much progress has made in increasing the scope of inorganic methods to include all the analytes of interest. Analyses can be performed more economically when only one sample preparation and one analysis technique are needed to fully evaluate a sample.

This work has demonstrated that mercury can be successfully determined in a digested TCLP extract matrix, as a part of the full suite of elements traditionally measured. Both ICP-OES and ICP-MS show excellent method detection limits for the elements measured and good predigestion spike recoveries with the exception of mercury. Further work is needed to define the mechanism for mercury loss in the digestion and transfer procedure used before the instrumental analysis.

Method 6010B for ICP-OES and proposed 6020A for ICP-MS contain the full list of analytes for TCLP analysis. This work validates the utility of these methods for this type of matrix. Microwave sample preparation procedures are especially useful when mercury is included in the analyte list, coupled with careful sample transfer and storage.

Acknowledgement

The authors would like to thank Bill Cyrus of the Trinity River Authority, Dallas, Texas for providing the TCLP extracts.

References

1. US Code of Federal Regulations 40, Ch. 1, Pt 136, Appendix B.

CLEAN METALS SAMPLING

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ABSTRACT

Scientific evidence[1] of aquatic organism toxicity to low concentrations of dissolved metals has led to the need for accurate and precise measurements of these compounds in a variety of aqueous matrices. A practical method[2] will be presented for the collection and analysis of freshwater and wastewater samples for trace metals. A hands on demonstration of clean techniques will be presented to show the simplicity and ease of collecting scientifically defensible samples for compliance monitoring purposes. Field sampling equipment specifications, collection procedures, the importance of blanks, and preservation of samples, will be discussed as topics important to designing a procedure for collecting water samples with metals concentrations in the range where toxicity is significant.

INTRODUCTION

To be protective of aquatic organisms and human health the US Environmental Protection Agency has established water quality standards[3], which specify safe concentration levels in background waters, for toxic metal species. Regulatory agencies must evaluate the concentrations of analytes in receiving waters and discharges to determine "reasonable potential" for impact to an ecosystem. Reliable methods for measuring trace concentrations of target compounds are essential to developing permit limits on discharges.

As regulatory levels for metals have decreased, sometimes several orders of magnitude, field collection protocols which are practical and applicable to a wide variety of site conditions and personnel must be developed.

The US Geological Survey (USGS) and the US Environmental Protection Agency (USEPA) have made progress in the last two years towards developing widely applicable field and laboratory procedures. The USGS has focused on internal procedures[4] designed to be used by USGS personnel. As a regulatory agency the USEPA has developed procedures[5,6,7,8,9,10,11,12] which can be used by monitoring groups, public agencies, and the regulated community.

The freshwaters appropriate for collection by this method include all surface waters and groundwaters with a specific conductivity of approximately 1000 umhos/cm or less. Appropriate wastewaters include treated effluents (conductivity < 1000 umhos/cm). Saltwaters, brackish waters, highly turbid wastewaters, i.e. landfill leachates, are not appropriate as they require special laboratory preparation and analysis.

The protocols contained in this Standard Operating Procedure are applicable to the compounds listed in Table 1 Target Analytes, Analytical Test Methods. and Detection Limits on page 8.

Additionally this SOP is suitable for freshwater and treated final effluents with concentrations of toxic metals below approximately 200 µg/L. The 200 µg/L threshold should be applied cautiously as this is only a generalization of the effect of contamination. For example, because of well documented contamination problems with copper and zinc, if a final effluent has historically had copper or zinc reported in the 0.2 mg/L range use of this protocol may reveal that the actual concentrations are significantly lower. However if the historical numbers for cadmium, arsenic, or mercury have been in the 0.2 mg/L range use of this protocol may not affect these concentrations. Another factor to consider when determining the applicability of this SOP is that typically the reporting level of historic data is much higher than the lowest concentrations when compared to Water Quality Standards.

For concentrations above approximately 200 µg/L, existing 40 CFR 136 procedures are adequate and contain the necessary Quality Controls (including the requirement to collect blanks) to make reliable measurements in the mg/L range. The United States EPA Region III has prepared extensive guidance for existing and new data which falls into this range.

METHODOLOGY

Improving on a combination of the more salient features from the USGS, USEPA, and others[4,13] the Virginia Department of Environmental Quality (VADEQ) began a pilot project designed to 1) determine if current technology could be used to accurately measure metal concentrations in water below 1.0 µg/L using clean techniques, 2) develop protocols for wastewater treatment plant effluent collection and analysis which could be incorporated into guidance and, 3) develop freshwater protocols for an ambient water quality monitoring program.

The main design considerations were to develop a system to 1) collect field samples free of contamination and, 2) minimize the level of effort required by field technicians.

When measuring at trace concentrations small amounts of background contamination and interference can be significant. The most likely sources of contamination are:

1. improper sample handling techniques,
2. improperly cleaned sampling equipment and sample containers, and
3. atmospheric dust and debris.

These ideas led to the design of a closed loop sample container which could be filled onsite, transported to the laboratory, prepared, and digested all in the same container. Figure 1 Loop Sample Bottle shows the container used to collect the samples.

Figure 2 Sample Collection Scheme illustrates the closed loop sample collection system. Sample collection is accomplished by pumping water from the sampling zone through a teflon tube, peristaltic tubing, and a capsule filter, directly into the loop sample container.

The entire process consists of the following steps:
1. Sample containers and tubing kits are cleaned and certified in a controlled laboratory environment.
2. The containers and kits are packaged into coolers and shipped to the field.
3. Blank ultra pure water from a blank sample container is processed through the tubing kit to condition and clean the capsule filter.
4. Ultra pure water from the sample container is pumped through the tubing assembly into the empty blank container to produce the field blank.
5. Sample is collected into the empty sample container using the tubing assembly.
6. Blanks and samples are shipped to the laboratory.
7. All samples and blanks are acidified, digested, prepared in the original container.
8. Samples are analyzed accordingly.

The advantage of this design is that field technicians receive the sample containers and equipment ready to use. Other than filter conditioning[14,15] there are no cleaning steps required and no need to preserve the samples other than icing. The sample containers include the water to be used for field blank collection with the blank collection exactly duplicating the site conditions of the sample collection. All the plasticware is inexpensive and can be discarded after single use.

DISCUSSION

Ambient Sample Collection Protocol

1. Locate an area where sample processing will occur. This should be an area free of falling debris and swirling dust, flat, smooth, and protected from the wind. The tailgate of a vehicle or the back of a Suburban are good locations.
2. Locate the equipment box and coolers containing the sample containers and kits in the area where sample processing will occur.
3. Cover the work area with a large piece of plastic film. Set out the pump and connect the battery. Switch pump on for a quick burst to check that it is working. Dial the pump speed to 5.
4. Remove a tubing kit, two sample containers, and a bridge bottle from the cooler and place on the plastic near the pump.
5. Remove a pack of sample gloves from the storage container and place on the plastic.
6. Remove the plastic sample caddie from the storage box and place it on the sample processing area near the pump. Secure the two sample bottles in the caddie.

Bridge Bottle Filling

1 . Locate the sample weights for connection to the BRIDGE BOTTLE.
2. Locate the polypropylene sampling rope spool, cut a sufficient length of rope to allow for deployment, and place on plastic.
3. Don one or two pairs of vinyl gloves using clean precautions.
4. Tie one end of the sampling rope to the five pound weight leaving approximately a 1' long end for connection to the BRIDGE BOTTLE.
5. Untie or open by tearing the top of the outer plastic bag containing the BRIDGE BOTTLE.
6. Reach into the outer bag and untie or tear the inner bag near the handle connection. Check the configuration of the tubing to ensure that proper filling will occur. While the bottle is still in the inner bag it is acceptable to remove the top fitting to check the inner sipper tube. Adjust all fittings appropriately.
7. When the fittings have been properly secured and adjusted remove the BRIDGE BOTTLE from the inner bag and lay on the plastic film. Tie the weighted end of the rope onto the handle of the bottle leaving about 6" of line between the bottle and the weight.
8. Proceed to the sampling location with the BRIDGE BOTTLE apparatus. If appropriate carry several extra pairs of gloves to the site to facilitate bridge bottle handling.
9. When deploying from bridges with moderate to low stream velocities collect the sample upstream of the bridge by lowering the assembly into the water. Ensure that the assembly does not contact any structures or other objects as it is lowered into the water.
10. Once in the water the weight will partially submerge the BRIDGE BOTTLE which will begin to fill. Check to insure the air release tube is above the water level and not obstructed. When the bottle is first submerged a good indication it is filling properly is a small slug of water may be expelled from the air vent tube. The bottle will fill quickly if it has been properly adjusted.
11. Problems with filling from bridges can occur when stream velocities are high. Sampling on the downstream side of bridges is acceptable to avoid the risk of losing the assembly due to the current sweeping it under a bridge or other obstruction. When stream velocities are high an additional 7.5 pounds of weight will aid in sample collection. The added weight will cause the container to sink lower when partially filled which may submerge the vent tube. The vent tube can be extended past the bottom of the bottle to prevent filling with water when the weight is heavy or the water is rough.
12. Other problems with filling can occur when the inlet tube is clogged, the vent tube contains a slug of water or other obstruction, the vent tube is below the surface of the water, the weight is not positioned close enough to the bottle, or the vent tube or inlet tube has become disconnected from the bottle.
13. When the BRIDGE BOTTLE is approximately 1/3 to 1/2 full retrieve the bottle and return to the sample processing area. Ensure that the assembly does not contact any structures or other objects as it is retrieved.
14. When deploying while wading or from a small craft the BRIDGE BOTTLE can be submerged by hand without the weights.
15. When the water level at the sample site is very shallow it may be difficult to submerge the BRIDGE BOTTLE deep enough to begin siphoning. The alternative is to use the effluent sample configuration where the stream sample is pumped directly into the loop sample container. Sampling in this manner requires the pump assembly to be transported to the site. This is best accomplished by attaching the pump assembly to a backpack.
16. Once the BRIDGE BOTTLE has been brought back to the sample processing area set it next to the pump and remove the weight. With the inlet and vent tubing properly configured the BRIDGE BOTTLE can remain on the plastic outside of a bag without any danger of atmospheric contamination.

Ambient Dissolved Grab Blank

1 . Refer to Figure 2 Sample Collection Scheme for the schematic of the field sampling equipment used to process blanks and samples.
2. Determine which tech will be clean hands and which will be dirty hands.
3. Dirty hands and clean hands don one or two pairs of vinyl gloves. Dirty hands opens the sample bottles outer plastic bag, clean hands opens the inner plastic bag.
4. Dirty hands opens the grab kit's outer plastic bag, clean hands opens the inner plastic bag and removes the tubing assembly.
5. Clean hands disconnects one side of the sample loop on a sample container. Clean hands connects the end of the tubing kit opposite the filter to the opened sample container. Remember the sample container is full of clean water from the lab.
6. Dirty hands connects the peristaltic tubing at approximately the mid-point of the length to the field pump, clean

hands inverts the sample container, and dirty hands switches on the pump.

7. Process the entire contents, 1000 mls, of the sample container through the tubing and filter apparatus at a flow rate of 500 mls/min. (pump setting of 5). At the beginning of the sample processing orient the filter cartridge with the flow arrow pointing up. This will insure proper wetting of the filter. After the last noticeable air bubbles have been expelled from the filter it can be oriented in any direction during the rinsing. When the sample container is nearing empty orient the capsule filter with the arrow down. Once the sample container is empty continue processing until the free water in the tubing and filter has been expelled.
8. Dirty hands turns off the pump. This step is a rinse of the filter which cleans and conditions the media. The rinse can be pumped directly to waste.
9. Use the same flow and orientation scheme throughout all sample and blank processing.

Field Blank

1. Clean hands removes the pump tubing from the empty bottle and connects the capsule filter to the empty container via the sample loop tubing. Remove one side of the loop fitting from a second sample container and connect the free end of the tubing to the container. Remember that this second bottle is full of clean water from the lab. Invert the container, dirty hands switches on the pump. Process the entire contents, approximately 1000 mls, of the sample container through the tubing and filter apparatus into the first sample container.
2. Dirty hands switches off the pump when the filter has been emptied. Clean hands disconnects the outlet tubing from the blank sample container and immediately reconnects the loop tubing, seals the inner bag and places inside the outer bag. Dirty hands identifies this as a blank by recording the ULTRA # as the CONTAINER ID, seals the outer bags, and places on ice in a sample cooler.
3. Clean hands immediately (immediately means the sooner the switch is made the less likely contamination can adhere to the end of an open tube, immediately means less than one minute) disconnects the tubing from the sample container and then connects the free end containing the filter, which was just removed from the blank sample container, to the empty sample container. Clean hands then disconnects the vent tubing from the BRIDGE BOTTLE and connects the pump tubing in place of the vent tubing.
4. The field blank collected in this manner is a comprehensive blank because it is collected in the same equipment as the sample and it is processed like the sample through all steps of the protocol. This is the most important check of contamination in the protocol.

Ambient Dissolved Grab

1. In a field notebook dirty hands records the sample container identification number, date, time. Clean hands secures the sample container in the sample caddie.
2. While keeping the BRIDGE BOTTLE near level dirty hands holds the bottle at the midsection or lower and shakes the vessel to ensure mixing. Dirty hands switches on the pump and clean hands collects a full sample container while following the filter orientation scheme. It is acceptable to fill the sample container to overflowing, however avoid filtering more than 1000 mls through the filter.
3. Once the sample container is full, dirty hands switches off the pump. Clean hands disconnects the outlet tubing from the sample container and immediately reconnects the loop tubing on the sample container, seals the inner bag and places inside the outer bag. Dirty hands identifies the sample by recording the ULTRA # as the CONTAINER ID, seals the outer bags, and places on ice in a sample cooler.
4. The clean protocol is complete at this step and field parameters can now be taken from the remaining water in the BRIDGE BOTTLE. Suggested field parameters include pH, Conductivity, Temperature, and Dissolved Oxygen. Additional laboratory samples for the solid series and total organic carbon should be prepared; group code SOLIDS, catalog number 190-243, and group code NME10. catalog number 190-25.
5. When finished with the BRIDGE BOTTLE seal the apparatus in a plastic bag and return to the cooler for recycling back to DCLS. DCLS will reclean, certify, and repackage for reuse.
6. Rinse the rope and weights with ambient water to remove any visible dirt, place inside a plastic bag, and store in the storage container. Rope may be reused several times if rinsed frequently.

Effluent Sample Collection Protocol

Equipment Setup

1. Locate an area near the final effluent sampling location where sample processing will occur. This should be an area free of falling debris and swirling dust, flat, smooth, and protected from the wind. The tailgate of a vehicle or the back of a Suburban are good locations.
2. Locate the equipment box and coolers containing the sample containers and kits in the area where sample

processing will occur.

3. Cover the work area with a large pick of plastic film. Set out the pump and connect the battery. Switch pump on for a quick burst to check that it is working. Dial the pump speed to 5.
4. Remove a tubing kit and two sample containers from the cooler and place on the plastic near the pump.
5. Remove a pack of sample gloves from the storage container and place on the plastic. Refer to, for the schematic of the field sampling equipment used to collect treatment plant grab samples.
6. Remove the plastic sample caddie from the storage box and place it on the sample processing area near the pump.
7. Locate the sample wand used for positioning the teflon sample tubing in the effluent.

Effluent Dissolved Grab Blank

1. Refer to Figure 2 Sample Collection Scheme for the schematic of the field sampling equipment used to process blanks and samples.
2. Determine which tech will be clean hands and which will be dirty hands.
3. Dirty hands and clean hands don one or two pairs of vinyl gloves. Dirty hands opens the sample bottles outer plastic bag, clean hands opens the inner plastic bag.
4. Dirty hands opens the grab kit's outer plastic bag, clean hands opens the inner plastic bag and removes the tubing assembly.
5. Clean hands disconnects one side of the sample loop on a sample container. Clean hands connects the teflon end of the tubing kit opposite the filter to the opened sample container. Remember the sample container is full of clean water from the lab.
6. Dirty hands connects the peristaltic tubing to the field pump on the end of the pump tubing closest to the connection with the teflon tubing. This allows for slack on the filter end of the pump tubing. Clean hands inverts the sample container, and dirty hands switches on the pump.
7. Process the entire contents, 1000 mls, of the sample container through the tubing and filter apparatus at a flow rate of 500 mls/min. (pump setting of 5). At the beginning of the sample processing orient the filter cartridge with the flow arrow pointing up. This will insure proper wetting of the filter. After the last noticeable air bubbles have been expelled from the filter it can be oriented in any direction during the rinsing. When the sample container is nearing empty orient the capsule filter with the arrow down. Once the sample container is empty continue processing until the free water in the tubing and filter has been expelled.
8. Dirty hands turns off the pump. This step is a rinse of the filter which cleans and conditions the media. The rinse can be pumped directly to waste.
9. Use the same flow and orientation scheme throughout all sample and blank processing.
10. Clean hands removes the teflon tubing from the empty bottle and connects the capsule filter to the empty container via the sample loop tubing. Remove one side of the loop fitting from a second sample container and connect the teflon end of the tubing to the container. Remember that this second bottle is full of clean water from the lab. Clean hands inverts the container, and dirty hands switches on the pump. Process the entire contents, approximately 1000 mls, of the sample container through the tubing and filter apparatus into the first sample container.
11. Dirty hands switches off the pump when the filter has been emptied as evidenced by air bubbles in the system. Clean hands disconnects the outlet tubing from the sample container and immediately reconnects the loop tubing on the sample container, seals the inner bag and places inside the outer bag. Dirty hands identifies this as a blank, seals the outer bags, and places on ice in a sample cooler.
12. This is a comprehensive blank because it is collected in the same equipment as the sample and it is processed like the sample through all steps of the protocol. This is the most important check of contamination in the protocol.

Effluent Dissolved Grab

1. In a field notebook dirty hands records the sample container identification number, date, time. Clean hands secures the sample container in the sample caddie.
2. Clean hands connects the filter to the empty sample container. Clean hands presents a section of the Teflon tubing just past the inlet to dirty hands who then attaches the tubing to the sample wand.
3. The entire assembly: sample caddie containing the empty sample container, sample tubing, pump/battery, and sample wand are transported to the effluent sampling location.
4. Dirty hands places the sample wand sample collection zone taking precaution not to touch the tip of the sampling tube on any items. Once the sample tube is located in the effluent take precaution not to let the tip contact anything but water.
5. Dirty hands switches on the pump and clean hands collects a full sample container while following the filter

orientation scheme. It is acceptable to fill the sample container to overflowing, however avoid filtering more than 1000 mls through the filter.

6. Once the sample container is full dirty hands switches off the pump. Clean hands disconnects the outlet tubing from the sample container and immediately reconnects the loop tubing on the sample container, seals the inner bag and places inside the outer bag. Dirty hands identifies the sample, seals the outer bags, and places on ice in a sample cooler.
7. The clean protocol is complete at this step and field parameters can now be taken directly from the effluent. Suggested field parameters include pH, Conductivity, Temperature, and Dissolved Oxygen. Additional laboratory samples for the solid series and total organic carbon should be prepared; group code SOLIDS, catalog number 190-243, and group code NME10, catalog number 190-25.

CONCLUSIONS

Using these clean procedures to collect more than two hundred samples the data indicate that collection of contaminant free samples at trace concentrations is possible. State regulatory agencies should be encouraged to move forward in promulgating guidance for trace element wastewater characterizations and ambient water quality monitoring. The careful application of the techniques developed by the U.S. Geological Survey and the U.S. Environmental Protection Agency can produce high quality data, satisfactory for regulatory decision making. By adopting the system of field procedures proposed here, investigations of water quality can be performed simply and cost effectively.

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Table 1. Target Analytes, Analytical Test Methods, and Detection Limits

Parameter	CAS Number	Method Detection Limits, µg/L				
		ICPMS USN	ICPMS USN TR	ICPMS	ICP AES USN	CVAA
Aluminium	7429-90-6		0.04	0.37		
Antimony	7440-36-0	0.05	0.03	0.33		
Arsenic	7440-38-2	0.07	0.03	0.24	5.37	
Cadmium	7440-43-9	0.06	0.04	1.72	2.37	
Calcium	7440-70-2				0.08	
Chromium	7440-47-3	0.02	0.04		2.27	
Copper	7440-50-8	0.02	0.06	0.87	4.98	
Iron	7439-89-6				2.3	
Lead	7439-92-1	0.17	0.03	0.28		
Magnesium	7439-95-4				0	
Manganese	7439-96-5	0.02	0.03	1.32	0.58	
Mercury	7439-97-6			0.12		0.07
Nickel	7440-02-0	0.04	0.02	0.39	1.71	
Selenium	7782-49-2		0.06	0.77		
Silver	7440-22-4	0.19	0.03	0.15		
Zinc	7440-66-6	0.26	0.03	2.18	1395	
ICPMS USN	inductively coupled plasma mass spectrometry sample introduction by ultrasonic nebulization					
ICPMS USN TR	inductively coupled plasma mass spectrometry sample introduction by ultrasonic nebulization total recoverable					
ICPMS	inductively coupled plasma mass spectrometry					
ICP AES USN	inductively coupled plasma atomic emission spectrometry sample introduction by ultrasonic nebulization					
CVAA	cold vapor atomic absorption spectrometry					

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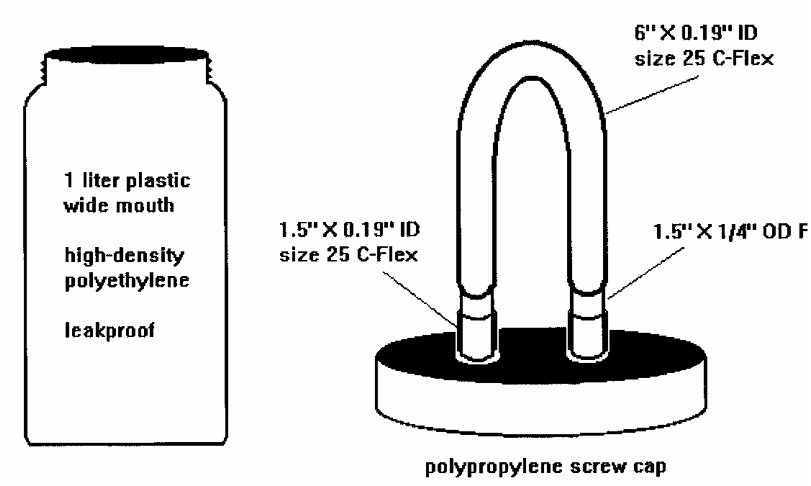

Figure 1. Loop Sample Bottle

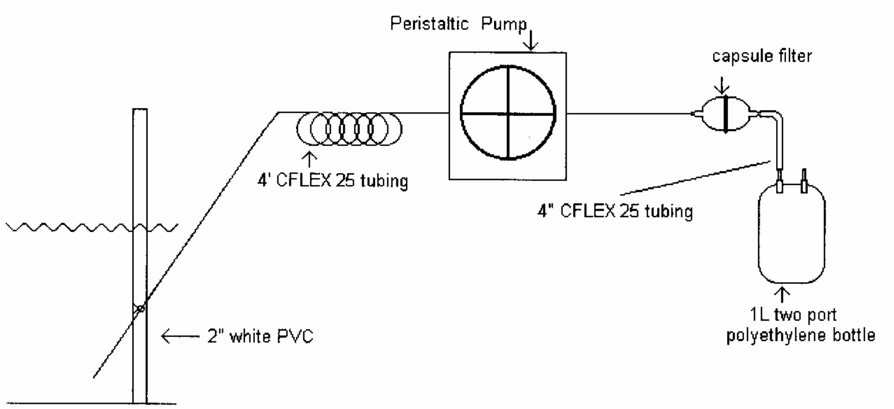

Figure 2. Sample Collection Scheme

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