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Technology Assessment of Field Portable Instrumentation for Use at Rocky Mountain Arsenal

Final Report

March 1988

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W. H. Griest
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EXECUTIVE SUMMARY

This work was initiated at the request of the U.S. Army Toxic and Hazardous Materials Agency for the purpose of reviewing the available literature and information base on field analytical instrumentation and analytical methods. One potential specific application of the findings of the assessment was the rapid deployment at Rocky Mountain Arsenal (RMA) of recommended approaches. Contamination at RMA is relatively well characterized, and the list of primary contaminants formed a starting point for this technology assessment. This report attempts to provide guidance with respect to a field analytical strategy which would be of general utility, to both this specific site and other areas which exhibit contamination of the type described. The classes of contaminants considered include selected metals, volatile organic compounds, and semivolatile organic compounds.

Sample preparation compatible with and practical for a field scenario is identified as a key issue. For the metals, all instrumental methods will require that the samples be digested to some extent in order to achieve the sensitivities required to determine all of the target elements at the concern levels. For this purpose, commercially available microwave digestion units appear to be a more mature technology, and are recommended, primarily because of reduced power consumption, increased sample throughput, and worker safety. However, dry digestion fluxes seem to hold considerable potential for near term deployment. For the volatile organic compounds, purge and trap and heated headspace techniques are recommended, with the purge and trap technique preferred on the basis of true portability and lowered detection limits. No real difference exists between the conduct of this method as it is suggested for use in the field and the way the technique would be employed in the laboratory. This would also be the case for the heated headspace technique. For the semivolatile organic compounds, the commercially available Soxtec extractor is recommended as the only device capable of being made portable and preparing soil samples for analysis in a reasonable time frame. A commercially available mixing device, the Mixxor, is recommended for the extraction of these compounds from water samples.

From the standpoint of analytical determination of inorganics in the field, x-ray fluorescence (XRF) is recommended as a screening system for those areas which are heavily contaminated. Once levels of contamination are achieved which are below the detection limits of XRF, colorimetric test kits could be used for screening the presence of lead and copper. Positive responses would then be followed by an accurate determination using a portable atomic absorption system. Arsenic and mercury would be determined by generating volatile species (arsine and mercury vapor), with quantitation performed using portable specific monitors. The best currently available technology for the organic compounds is gas chromatography using a portable unit for determination of volatile constituents, and a small rugged laboratory unit for which power is supplied by a small portable generator. Other, less mature technologies are identified which merit serious development effort in the future.

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BACKGROUND

In the Department of Defense's (DOD) facilities around the world, there exist a number of sites which have been contaminated with one or more toxic inorganic or organic chemical species. The Program Manager, Rocky Mountain Arsenal has been charged with the restoration of Rocky Mountain Arsenal (RMA), near Denver, Colorado. The responsibility of the U.S. Army's Toxic and Hazardous Materials Agency (USATHAMA) is to provide chemical support to that effort. Much of the clean-up effort, both at this and other DOD sites, will be directed toward the remedial excavation of areas which are contaminated with specific toxic or hazardous compounds above some defined limit. With the current situation, field sampling, followed by laboratory analysis of various samples, would direct the restoration activities. While detailed laboratory analysis is an appropriate approach for determining the overall extent and nature of contamination at a number of sites within the reservation, such an exhaustive and time consuming approach is not particularly desirable for directing restoration activities. In the latter case, a rapid, accurate determination of the levels of selected target species, with an emphasis on minimizing sample turnaround time, seems much more appropriate for guiding restoration activities.

Oak Ridge National Laboratory (ORNL), as part of a project to implement cost effective field strategies for the determination of target constituents in environmental samples collected at RMA, was requested to conduct an assessment of the current, commercially available analytical technology as it would apply to more rapid, cost effective, analysis of target species. This report is the product of that assessment. Promising approaches requiring some amount of development are also identified and described.

Ideally, such analyses would be conducted with completely portable systems in the field. Recognizing that in many cases, truly portable field analysis may not be possible, attention has been given to both field mobile systems (i.e., those that can be operated in a field situation but require utilities, such as air conditioning, power, large amounts of solvents or compressed gases) and methods and/or systems which would provide for more rapid turnaround or sample throughput in a conventional laboratory or large mobile van.

Monitoring Requirements: There are a large number of toxic species, both inorganic and organic in nature, which have been identified in environmental samples. To provide an adequate assessment of appropriate technologies for all of the toxic contaminants would be a monumental task. For the purposes of this technology assessment, we were instructed to focus primarily on the "target" constituents listed in Table 1. However, some discussion is directed toward other toxic constituents likely to be present in the matrices. These may represent significant interferences to the determination of the target constituents, or may eventually be given "target compound" status themselves. The "concern levels" listed in Table 1 are those which were provided by PM/RMA and have no particular significance, legal or

otherwise. The target species were selected with the guidance of PM/RMA following a review of data obtained during contamination assessment surveys of the Arsenal. However, recommendations as to appropriate field technologies are to be considered generic to any site where such contamination exists, and should be applicable to both remedial action and site investigations.

Table 1

Target Toxic Contaminants for Technology Assessment

	Concern Level	
	Soil (μg/g)	Water (μg/L)
Inorganic Constituents		
Copper	100	500.0
Lead	10	25.0
Arsenic	1.0	10.0
Mercury	100	0.5
Organic Constituents		
Benzene	0.01	1.0
Trichloroethylene	0.10	1.0
Tetrachloroethylene	0.01	0.5
Dicyclopentadiene	1.0	10.0
Dibromochloropropane	0.001	0.025
Diisopropylmethylphosphonate	100	100
Aldrin	0.004	0.005
Endrin	0.1	0.1
Dieldrin	0.0005	0.005

This report is organized according to specific areas of technology. However, because of commonality in sample processing techniques, methods for detection, etc., there is some overlap of some discussion sections. Recommendations for the most appropriate approach using the technology described are provided at the conclusion of each section. Summary recommendations, concerning the most appropriate overall approaches are given at the end of the inorganic and organic chemistry sections.

INORGANIC SPECIES: INTRODUCTION AND SAMPLE PROCESSING

As will be indicated in the assessment below, with the exception of the use of x-ray fluorescence (XRF) for the analysis of particularly contaminated samples, all of the technologies for the determination of the target species require some digestion (ie. chemical processing) of soil or water samples prior to instrumental or colorimetric determination. Because the procedures are so chemically rigorous, the digestion has the effect of masking the original valence state of the element. In cases where the valence state is important to the relative toxicity of the species, (chromium VI vs. chromium III, or metallic mercury vs. organo alkyl mercury), this is an unfortunate consequence. However, there are some practical reasons as to why chemical processing in a field scenario is likely to be conducted with little regard to the original valence state of the element. First, the immediate environment of the species may control the valence, so that the act of isolation of the element or compound from its surroundings, regardless of chemical processing, may alter the valence anyway. Secondly, processing of a species so as to preserve the original valence may require much more sophisticated chemical manipulation than that which can be conducted conveniently in the field. Finally, in most cases, regulatory decisions or risk assessments are not made on the basis of valence state. Often, allowable quantities are established assuming the most toxic state of an element is present.

From a practical standpoint, probably the most difficult aspect of the field analysis of inorganic species is the processing of the sample prior to instrumental determination. It typically involves the use of caustic or corrosive chemicals and a requirement of heat for relatively long periods of time, which in turn necessitates the presence of direct thermal energy or electrical power. To determine lead and copper in soil samples by ICP or AA, or to measure them by XRF at the concern levels, it is necessary to chemically extract them from the solid samples and prepare them in the appropriate form for analysis. For analysis by ICP or AA, the appropriate form for an analysis is a solution without solids. Soil samples would likely be treated according to a procedure similar to Method 3050 of the EPA publication SW-846, "Test Methods for Evaluating Solid Waste." Method 3050 pertains to the digestion of sediments, sludges, and soils with nitric acid and hydrogen peroxide for analysis of toxic elements in Resource Conservation and Recovery Act (RCRA) wastes. This procedure involves repeated digestion with nitric acid at boiling or near boiling temperatures, followed by evaporation, and subsequent reaction with hydrogen peroxide. The sample manipulation is likely to require two to three hours to complete. Typically, water samples would be treated by a nitric acid digestion procedure similar to that described in USATHAMA method B-8. This too involves a rather lengthy digestion/evaporation sequence at elevated temperatures. Following dilution and filtration, the samples are then ready for analysis by ICP or AA.

Processing for arsenic and mercury is somewhat less generic, in order to reduce the probability that these elements would be converted into

their most volatile forms and be lost during digestion. The specifics of these processing steps are described in detail in the section dealing with arsenic and mercury determination by vapor generation.

While these procedures can be conducted in the field by, for example, supplying thermal energy from a camp stove, their labor intensity and time consumption are a serious impediment to practical rapid determination to the target species near the concern levels. In addition, the use of a large continual open flame heating system is much less desireable from a safety standpoint. One approach to the need for more rapid sample processing which has received considerable attention lately is the use of elevated pressure microwave induced digestion (1). There is one system commercially available. In this system, the sample is mixed with the appropriate acid, sealed in a Teflon bottle, and placed in the heating compartment of a rugged microwave oven for a specific power and time. Typically, the use of such a system reduces multi-hour digestions to less than one hour. In addition, the microwave approach has at least two advantages beyond those of reduced time. First, it minimizes the handling and consumption of acids, reducing bulk and worker exposure. Also, the increased speed ultimately reduces the amount of power needed in the field. To be sure, the commercially available system is not portable in the truest sense. The CEM Model MDS-81D weighs about 36 kg, and requires a maximum of 15 amps at 110 vac. However, this can be easily supplied by a gasoline powered generator, and the time and safety considerations easily compensate for the additional bulk and weight. Sample size is limited to 500 mg for soils and 50 mL for waters. Above these levels, the amount of organics in a sample can produce excessive amounts of evolved gas in the vessel. However, most of the analytical methods described below have sufficient sensitivity that the small sample size should not be a problem.

Two other approaches to the extraction of inorganic species from soil matrices appear promising, but are likely to require some developmental effort. One approach, utilizing extraction via a mild acid, such as acetic, assumes that there is no interest in determining the inorganic content of the minerals in the soil, only those which are anthropogenic in origin. Extraction with acetic acid mimics more closely those processes which occur in nature, and thus may have greater relevance to assessing the extent to which contamination in, for example, soil, would migrate into the groundwater. The second approach to facile extraction in the field utilizes a material recently introduced by Scintrex Corporation, the makers of a field mobile atomic absorption unit (see below). The material is a low temperature flux, called Geoflux. The proprietary mixture is used by adding a gram of dry, crushed soil to six grams of flux, and heating in a glass test tube for about five minutes over a propane torch. An exact procedure has been developed for the determination of gold, cadmium, nickel, zinc, and lead. Presumably, it would not be difficult to work out similar methods for the dry fusion of the remaining target metals, with the exception of mercury.

Initial sample preparation for XRF analysis of low level contaminants would be essentially that described for lead and copper above. In order to extend the normal detection limits of XRF, elemental species would have to be collected in solid form and concentrated in a relatively small volume. One approach to preparing the sample is to precipitate the elements of interest or co-precipitate them with an added metal ion with a suitable reagent. If chromium and arsenic were adjusted to a valance of +3, then it should be possible to precipitate together all of the elements of Table 1. One study has shown that nanogram quantities of the transition elements at a pH of 3.8-4.5 can be co-precipitated with 2 micrograms of Ti^{+4} using the reagent sodium diethyldithiocarbamate and the precipitate recovered in a 1.27 mm diameter spot on a cellulose filter (2). The transition elements were then measured by x-ray microprobe in which an x-ray beam was focused only on the precipitate. By using this pre-concentration, the method of x-ray fluorescence was extended from the range of 10-100 ppm to 1-100 ppb. A similar approach to measuring the elements of Table 1 that exist in a treated water sample or are recovered from soil would probably be satisfactory. The reagent diethyldithiocarbamate will precipitate Cu^{+2}, Cr^{+3}, Zn^{+2}, Cd^{+2}, Hg^{+2}, and Pb^{+2}. With the addition of sulfide it should be possible to also precipitate As^{+3}.

Recommendations

Given the difficulties and lengthy times required for classic hot plate type acid digestions, and worker exposure to acid fumes, the use of such methods can be recommended only for those situations in which electrical power (to drive a microwave digestion system) can not be provided. In such a case, there would remain some safety concerns about the use of long duration open flames. Otherwise, the use of a microwave system appears to be the method of choice. Of course, some effort will be required to establish the best digestion conditions for the elements of interest in the appropriate matrix. However, it should be possible to build on the many studies currently in progress which are addressing such considerations. Also, for XRF detection limit extension, some effort would be required to optimize the configuration of the co-precipitate on a filter, so that it would have maximum compatibility with the measurement head of a portable XRF unit. The use of more gentle means of extraction of the target analytes, such as weak acid extraction or low temperature fluxes, appears promising. However, some developmental effort would be required to bring these methods into operational viability.

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COLORIMETRIC METHODS

Background

The technique of using the color of specific elements or their compounds for quantitative determination has been known since ancient times (1-4). In the middle of the last century, the prototype for colorimetric instrumentation was developed. Since then, colorimetric analysis (colorimetry) has become one of the most frequently used analytical techniques. Typically, the instrument used for colorimetry is equipped with a monochromator and a photocell detector, therefore a more appropriate description of colorimetry might be "visible wavelength spectrophotometry." The concept of colorimetry is based on the absorption of visible light by a colored solution (1-4). The amount of light absorbed is proportional to the concentration of the colored species in the solution. Thus, the amount of absorbing colored substance can be quantitatively determined. In general, to determine an element colorimetrically, it is converted into a colored complex by reaction with a specific organic reagent. This provides enhanced selectivity and sensitivity, which is further enhanced by the use of a specific wavelength of visible light for the actual determination.

A tremendous number of colorimetric methods have been documented and routinely used for determining most of the elements and many types of organic compounds. The discussion below will focus on the most appropriate colorimetric procedures for the target inorganic species.

The Environmental Protection Agency (EPA), the National Bureau of Standards (NBS), and the Standard Methods Committee (SMC) have suggested that atomic absorption (AA), colorimetry, and inductively coupled plasma (ICP) are the standard laboratory techniques for measuring the metal content in aqueous or soil samples (5-8). Since the portable instrumentation for colorimetry (see below) is far simpler and less expensive than those of AA and ICP, the application of colorimetry for the field determination of target elements bears consideration. Metals existing in samples (aqueous or soil) can be present as various inorganic or organic species, or in dissolved or suspended states (in aqueous samples). Since the speciation of the inorganic species may depend on its immediate chemical environment, the determination of the total concentration of each metal present is usually more practical. For the field determination of the target species, the sampling and chemical processing procedures reported by the EPA, NBS, and the SMC for measuring As, Cu, Pb, and Hg (5-8) could be used, while portable instrumentation would be substituted for a conventional laboratory UV/visible spectrophotometer.

Approach and Evaluation

Procedures for determination of each metal can be briefly summarized as follows:

Arsenic (6-8): The sample is first digested in a non-reducing environment, and arsenic in the sample is reduced to arsine, AsH_3. The arsine is passed through a scrubber containing glass wool coated with lead acetate to remove sulfide and is absorbed in a solution of silver diethyldithiocarbamate dissolved in pyridine. The resulting red complex would be measured using a portable spectrophotometer with the wavelength set at 535 nm. The calculation of As concentration in the sample is determined from a standard curve. The limit of detection for the method is about 1 μg absolute, which would translate to 2 μg/g soil for a 500 mg sample, or about 20 μg/L for water samples, assuming a 50 mL sample size. These detection limits are a factor of two above the concern levels stated in Table 1, suggesting that this approach may not be appropriate for arsenic determination. However, it would seem a relatively simple matter to increase the sample size by a factor of two or three by compositing samples.

Antimony may interfere with the determination of arsenic. Antimony in the sample forms stilbene (SbH_3) which reacts similarly to arsine (AsH_3) with silver diethyldithiocarbamate. The absorbance maxima of the two colored products are different (μ max for Sb = 505 nm; μ max for As = 535 nm). If only arsenic is present, the 505/535 absorbance ratio will not exceed 0.80. If this ratio is greater, the correction can be made for As by using simultaneous equations, since the absorbance of these two colored products are additive at these two wavelengths. Several other metals are listed as interfering with the arsine generation process. These include chromium, copper, cobalt, mercury, molybdenum, nickel, platinum, and silver. The fact that many of these metals may be present in contaminated soil suggests that interference evaluation studies must be performed using the matrix of interest prior to the use of this colorimetric procedure in the field.

There appear to be no commercially available colorimetric test kits for arsenic.

Copper (8): The sample is first digested with H_2SO_4/HNO_3 and copper is reduced to its cuprous form, which in turn is reacted in a neutral or slightly acidic solution with neocuproine (2,9-dimethyl-1,10-phenanthroline) to form a yellow complex. The complex can be extracted by a number of organic solvents, including $CHCl_3$ and chloroform-methanol. The extract can be measured in a portable colorimeter or spectrophotometer at 457 nm. The calculation of Cu concentration in the sample is based on a standard curve. The limit of detection using a 1 cm optical path length cell is about 3 μg copper. This translates to about 6 μg/g soil for a 500 mg sample, and about 60 μg/L for a 50 mL water sample. These detection limits are well below the concern levels listed in Table 1. Large amounts of chromium and tin may interfere with this procedure. Interference from chromium can be avoided by adding sulfurous acid to reduce chromate and complex chromic ions. Interference from tin can be reduced by adding excessive $NH_2OH \cdot HCl$.

There are also a number of commercially available test kits for copper. Two are marketed by the Hach Chemical Company. One of these appears

sufficiently sensitive to be of utility in a field monitoring situation. The method is based on the complexation of copper by porphyrin, and has the primary advantage of requiring no extraction of the colored complex with organic solvents. Details of the procedure can be found elsewhere (11). Briefly, the digested sample is reacted sequentially with two reagent "powder pillows", and the resulting color quantitated spectrophotometrically. The limit of detection appears to be about 1 μg/L for water samples, with an upper limit of linearity of about 225 μg/L. For soil samples, the amount of sample digested can be altered appropriately.

Another commercially available approach to the semi-quantitative determination of copper is the use of colorimetric test papers. Gallard-Schlesinger Industries markets a QUANTOFIX brand of test sticks, one of which is appropriate for the determination of copper as Cu^{+} or Cu^{+2} between 0 and 1000ppm. These materials are similar to pH paper, and they turn from white to red-violet. The cost is about $12 for 100 sticks.

Lead (8): The sample is first digested using HNO_3 and mixed with ammoniacal citrate-cyanide reducing solution. The lead is subsequently extracted with dithizone in $CHCl_3$ to form a cherry-red lead dithizonate. The color of the complex is measured in a portable colorimeter or spectrophotometer at 510 nm. The calculation of Pb concentration in the sample is determined from a standard curve. Bismuth, stannous tin, and monovalent thallium may interfere, since those elements form colored complexes with dithizone solution. Excessive quantities of those elements can be removed by subjecting the sample to an ASTM processing step, which consists of extraction of the lead dithizone complex at a higher pH(9). (The interfering complexes of bismuth, etc., are not stable at a pH of 11.0). Divalent copper, cadmium, and mercury, and trivalent arsenic and iron do not interfere. The minimum detectable concentration of lead by this method is 1 μg/10 mL of dithizone solution. However, as much as 2 L of sample water can be handled in the digestion step, if it were performed outside the microwave digestion system. This translates to a sensitivity of 0.5 μg/L for water samples, or 2 μg/g for 500 mg soil samples, which are below the concern levels listed in Table 1.

Another approach to the determination of lead in a field setting is the use of a small test kit marketed by Frandon Enterprises of Seattle. The kit is sold as a rapid screening tool for the detection or lead in glazed earthenware pottery. The method is based on the dithizonate method described above (albeit with streamlined reagent preparation and processing for ease of use by consumers), while the extraction of the pottery is performed using warm vinegar (acetic acid). Presumably, the test kit based procedure would be subject to the same sorts of interferences as the detailed method described above. No information was made available as to the limits of detection or linear range of the test kit. However, it would not be expected to be significantly different from that of the original method.

Mercury (8): The sample is first digested with a weak solution of HNO_3. Mercury ions react with a dithizone solution in $CHCl_3$ to form an orange complex. The color of the complex can be measured in a portable colorimeteror spectrophotometer at 492 nm. The calculation of Hg concentration is based on a standard curve. The minimum detectable concentration is 1 μg/ 10 mL final volume, which corresponds to 2 μg/g soil, or 20 μg/L when a 50 mL water sample is used. This latter level is a factor of 40 higher than the target concentration limit for mercury in water. These data would indicate that a colorimetric analysis for mercury in water would be clearly inadequate to meet the concern level in water, and would require an increase in sample size to reach the concern level in soil. Copper, gold, palladium, divalent platinum, and silver may interfere with this procedure. Copper usually can be separated from mercury, since in the dithizone extraction process, copper remains in the organic phase while the mercury dissolves in the aqueous phase. Noble metals (gold, palladium, platinum, and silver) would not be expected to be present in high concentrations in waste samples.

No prepackaged test kits were determined to be commercially available for mercury.

While it is strictly designed for use with neither inorganic species nor any of the target organics, a colorimetric test kit which bears mention has been very recently marketed by the Dexsil Corporation. It is a two stage kit designed to determine the presence of polychlorinated biphenyls in soil at a range of 1-50 ppm. In the test kit, the soil sample is first extracted, in order to separate the PCB's from the free chloride in the soil. Next, the PCB containing extract is reacted with sodium metal, in order to digest the PCB's and free the chloride. Next, the chloride is reacted with a dye, the intensity of the ensuing color being inversely proportional to the amount of PCB's originally present. Such a kit may also be of utility for screening the presence of chlorinated pesticides or solvents.

Although all of the procedures described have been originally directed toward the determination of target species in aqueous samples, the first step of sample preparation is always a digestion process (with inorganic acids and heating). With such vigorous reaction conditions, metals in soil samples can be extracted into an aqueous system. Thus, by a small modification, all documented procedures for aqueous samples should be suitable for analysis of soil samples.

Typically, 2-3 hours are required for sample processing and analysis of a particular sample for one metal (including sample preparation and standard curve determination). Use of microwave digestion procedures (10) in a field setting could reduce the initial sample processing time substantially. Such would require the provision of ac power in a field setting. However, given the low power requirements of a microwave oven (less than two kilowatts), the use of an inverter or small generator should represent few difficulties. CEM corporation markets a small microwave digestion system (MDS-81D) which uses a combination of

microwave heating and Teflon pressure vessels to permit the digestion of environmental samples at elevated temperatures. The higher temperature/pressure regime results in dramatically reduced digestion times.

The instrumental requirements for the field determination of these species are relatively simple. Any of the common UV/visible spectrophotometers found on the market can be used for colorimetric determinations. However, since most of the commercially available UV/visible spectrophotometers are designed for laboratory use, the instruments are heavy (more than 30 kg), and require ac power, which is less desirable for field use (5). Recently, Hach Chemical Company has marketed two portable instruments for colorimetric analysis. The Hach DR 100 colorimeter or Hach DR/3 single-beam spectrophotometer are suitable for field use (5). The important characteristics of these two instruments are summarized below:

Instrument	Hach DR 100 colorimeter	Hach DR/3 single-beam spectrophotometer
Mode of operation	%T, absorbance and concentration	Absorbance, %T and concentration
Wavelength	420, 450, 500, 525, 550, 575, and 610 nm	Variable, between 325-1000 nm
Power requirement	4 AA alkaline cells	4 D-cell alkaline batteries
Dimensions	11 cm H x 31 cm W x 20 cm D	18 cm H x 44 cm W x 48 cm D
Weight	4.5 kg	12.9 kg
Price	$195	$895

Clearly, the Hach DR 100 colorimeter would be easier to carry for field use, but its limited wavelength selection reduces its versatility.

In summary, there are a number of advantages in using colorimetric methods for determination of Hg, As, Pb, and Cu in a field scenario:

1. The overall technology is relatively mature and well-understood.

2. Colorimetric instrumentation or spectrophotometers are simple, small, lightweight, operated with batteries, and inexpensive.

3. Precision and accuracy are relatively high.

4. Procedures for sample preparations have been thoroughly investigated by regulatory agencies.

5. Minimum detectable quantity is about 1 μg, and in many cases, the sensitivity level meets or exceeds those of the concern levels.

6. Selectivities range from moderate to very high.

7. Rapid sample screening could be performed.

Some limitations of colorimetry for measurement of the target species are:

1. Compared to other instrumental methods, samples determined by colorimetry have to be subjected to a more complicated preparation procedure. This may require field personnel whose chemical manipulation skills are relatively sophisticated.

2. Determination of more than one metal on a single sample is not possible.

Recommendations

The use of colorimetry in a field setting is potentially attractive, because of the simplicity of the analytical instrumentation involved. However, it also has a number of drawbacks. First, in a situation where potential matrix interferences are not well understood, there may be a number of substances present which could yield false positive results. More importantly, even after performing the digestion procedures (which is mandated for nearly all of the analytical procedures being considered in this assessment), the samples must undergo reasonably complex processing. This latter requirement is somewhat obviated when using the commercially available test kits. It would appear that the most appropriate approach would be the use of the commercially available test kits for copper and lead as screening systems. If positive results were obtained, the samples could be subjected to more sophisticated (and time consuming, but less interference prone) procedures, such as those described elsewhere in this manuscript.

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INSTRUMENTAL ANALYSIS OF VOLATILE FORMS OF ARSENIC AND MERCURY

Background

The determination of arsenic and mercury in a field setting poses an interesting analytical challenge. While it is possible to determine arsenic or mercury by many instrumental techniques, great care must be taken not to produce the volatile forms of these elements (either the arsenic hydride - arsine - or elemental mercury -Hg°) in an open system during chemical processing because of potential losses due to volatility. However, this volatility can be exploited for the determination of these species. For example, by generating elemental mercury under controlled conditions, the absorption of Hg vapor can be used to quantitate its presence in the matrix of interest. The so-called "cold vapor" method is widely used by regulatory agencies for its determination in environmental samples, but requires a spectrophotometer for ultimate quantitation. Also, once sample digestion has occurred, arsine can be easily generated using a mixture of reagents. (Although a packet is available commercially, the reagent mixture is so simple that it can be easily prepared in the laboratory). Below are described a cold vapor generation technique to be used in combination with a unique portable Hg monitor, and a hydride generation method to be used in combination with a portable arsine monitor. Either of the two systems appears suitable for use under field conditions.

Approach and Evaluation - Mercury

Method 7471 in the EPA Manual 846 describes a procedure for the extraction of mercury from solid or semi-solid waste samples and its measurement by atomic absorption using a cold vapor (CV) technique to evolve the mercury. The overall procedure is quite similar to USATHAMA Method V9. The sample is digested for two minutes at 95°C in a 1:1 combined solution of water and aqua regia to extract Hg. After the sample is cooled, a solution of potassium permanganate is added, and the solution is reacted at 95°C for 30 minutes to oxidize sulfides to sulfates and prevent their interference in the Hg measurement. The excess permanganate is reduced with a solution of hydroxylamine sulfate, and a solution of stannous sulfate is added to reduce Hg^{+2} to elemental mercury. Mercury vapor can then be evolved with an air stream that is circulated through the solution and an AA absorption cell in a closed system and measured by atomic absorption as described in Method 7471. Of course, elemental mercury in a liquid system can be easily evolved simply by purging the system with an air stream. It has been found that the sensitivity of the CV technique can be extended significantly by evolving the mercury vapor onto silver wool which captures the Hg vapor as an amalgam (1,2). The mercury is subsequently thermally eluted from the silver wool and measured by AA. A detection limit of 1 ng has been determined (1,2).

This approach ultimately requires quantification using an AA system, and there are a few small systems on the market which amount to small,

dedicated, AA analyzers for mercury vapor. However, these systems require external power, and thus their utility in a field setting may not be as universal as that of a system based on a final analytical determination employing a hand held instrumental monitor. The latter monitor's function is based on the amalgamation of airborne Hg^o with gold. The electrical resistance of the film increases linearly with the mercury concentration in the gold, and the resistance can be measured to determine the quantity of mercury that has plated out on the film. This principle is employed by the Jerome Instrument Corporation (JIC) in several devices that contain a patented gold-film mercury monitor. The Model 411 gold film mercury analyzer is portable and operates on a 7.2 volt rechargeable battery pack. It will detect 1 ng of mercury, and appears to be sufficiently rugged for field use. This translates into a sensitivity of 1 ng/g soil using a 1 g soil sample size and a 1 L/minute purge rate, 20 ng/L for a 50 mL water sample. The experimental arrangement of such a configuration is depicted in Figure 1. Cost of the Jerome instrument is approximately $4500, depending on what optional accessories are purchased. In a field situation, the JIC Model 411 could easily replace a much more complex AA measurement system. The digestion heat could be supplied through a small gas heater (although there may be some concerns about the safety of open flames), and the air purging provided by a small, battery-powered industrial hygiene sampling pump.

Approach and Evaluation - Arsenic

The generation of the trivalent arsenic hydride - arsine - is a common method for the quantitative determination of AS in environmental samples (3). Following digestion of the sample (in a non-reducing atmosphere so as to prevent the premature loss of AS), the digestate is mixed with stannous chloride and metallic zinc - the so-called Gutzeit reaction. Arsine evolves as the reaction product, and can be quantitated using various colorimetric reactions or atomic absorption spectrophotometry. A variation of the Gutzeit reaction used in conjunction with colorimetric detector tubes (4) or a portable instrumental arsine monitor has the potential for deployment in a field setting. In the modified reaction, the digested sample is reacted with a prepackaged mixture of 1 g of powdered zinc and 1 g of potassium bisulfate containing a crystal of cupric sulfate as a catalyst. The reaction is conducted in a jar to which is affixed an arsine detector tube (4). The resulting effervescence scrubs the arsine from the solution through the tube. If a greater degree of control over the flow rate were desired, a small personal monitoring pump could be attached to the downstream end of the detector tube.

The tubes are sensitive to arsine over a range of 0.05 ppm to 60 ppm. This would translate to a sensitivity of about 75 ng/g soil, or 0.75 μg/L for a 100mL water sample, assuming a sampling of 500mL of air through the detector tube over a five minute period. The tubes are not noted for their accuracy, but such an apparatus would be quite useful for screening purposes. A similar but more quantitative approach would

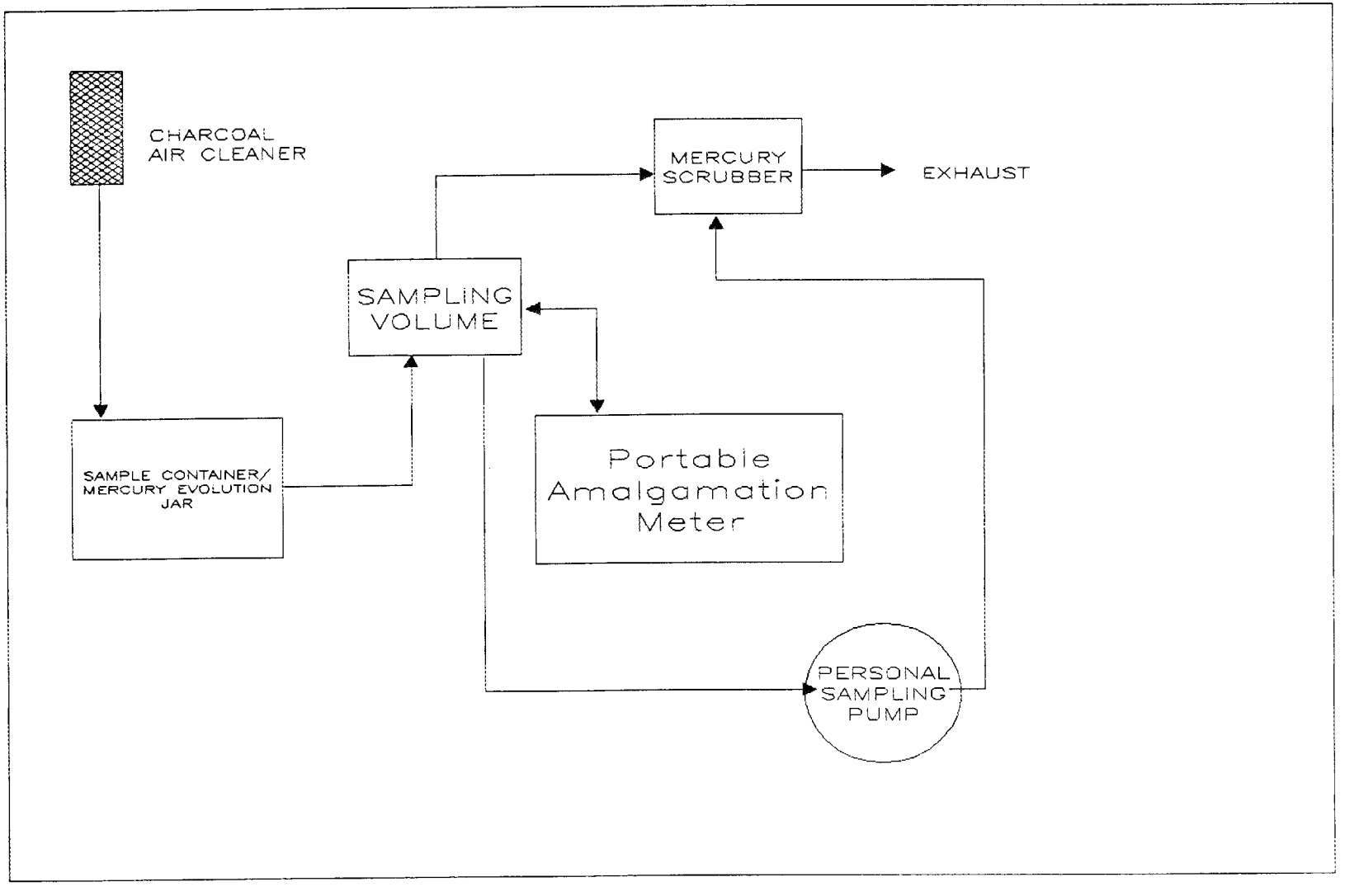

Figure 1. Schematic Diagram of Field Mercury Vapor Generation/Analysis Apparatus

substitute a portable instrumental arsine monitor for the detector tube/pump arrangement. This would be quite similar to the arrangement for mercury evolution depicted in Figure 1. The Sensidyne Model SS4000 Arsine Monitor is small (2Kg), has a battery life of 35 hours, and a built-in sampling pump. The system's operational principle is based on electrochemical detection. The manufacturer claims an accuracy of ±8%, and the system has a dynamic range of 0-1 ppm or 0-5 ppm. Cost of the unit is about $3300. Another portable system is the Riken Model AS-7 ($2000), which is also self-contained, and possesses a linear dynamic range of 0-1 ppm. Clearly, these devices do not possess as large a dynamic range as the detector tube. However, sample size could be adjusted appropriately, especially if the arsine generator/color tube combination was first used as a screening system.

Recommendations

The generation of volatile forms of mercury and arsenic, followed by instrumental analysis using portable systems, appear particularly promising for analysis of these constituents. While both require sample digestion, the digestion appears no more complex than would be required for analysis using atomic absorption as the final step. Presumably, microwave aided digestion could make the sample processing system much simpler and less time consuming. The instrumentation is portable, sensitive, and relatively inexpensive. It is recommended that these approaches be included in the final recommendations describing the most viable likely approaches for fieldable analytical technology.

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CONVENTIONAL ATOMIC ABSORPTION ANALYSIS

Background

Atomic absorption spectrophotometry, usually called atomic absorption (AA) is a highly sensitive tool for trace element analysis in use in most modern analytical chemistry laboratories. The salient features of the method, both in principle and practice, have been discussed in detail elsewhere (1,2). A detailed discussion of AA and its use in soil analysis is presented in reference 3, while L. de Galan has discussed recent advances in AA (4).

Atomic absorption is based on the principle that gaseous atomic species absorb light at frequencies characteristic of their electronic structure. Light is radiated through a region, either in a flame or a furnace tube, into which atomic vapor has been evaporated, and light having the frequency (wavelength) in resonance with the electronic structure of the atoms is absorbed. A basic AA system consists of a light source, a flame or furnace for generating the atomic vapor, a monochromator, and a light measuring device, e.g., a photomultiplier tube. From the energy source that causes the evaporation come the terms flame and furnace AA. A graphite tube furnace is ordinarily used in furnace AA. Normally the light comes from a very special source, a hollow cathode lamp that contains some of the element whose assay is desired. In this way light of the correct wavelength is selected and the intensity of the other wavelengths is minimized.

The emission of radiation from the hot analyte contributes to the background observed with AA. And because other species absorb, scatter, or otherwise decrease the light intensity at this wavelength, the method exhibits a background level even if there are no atoms of the desired element present. Because of the unstable and non-reproducible nature of the heated atomizer, the background cannot be corrected by the double beam method that is used in other types of spectrophotometry. However, a number of ingenious methods have been developed to correct for the background emissions. One of the most successful background correction methods makes use of the Zeeman Effect, which has been described in detail elsewhere (1).

Approach and Evaluation

To be analyzed, a sample must be in a liquid form, and in some circumstances a chemical separation must be performed to eliminate interfering chemical species before a desired analysis can be effected. Typically, samples are introduced into flame AA instruments for analysis by aspirating the liquid sample. In furnace systems, a small liquid sample, usually a fraction of one mL, is added slowly, dried, and then atomized. The extraction of trace elements from soil and the preparation of samples for AA is a rather time consuming process. The acid extraction of trace metals from soils has been discussed briefly in a previous part of this report. In Page's compilation of analytical methods for soil are presented methods similar to EPA SW-846 procedures

for the dissolution of soils and the determination of all the elements of Table 1 by AA. In contrast, most water samples can be analyzed directly with little or no chemical treatment.

Both portable and laboratory AA systems are available commercially. Perkin-Elmer markets a "portable" atomic absorption unit with an automated sample processing system. The device sells for about $60,000 and is referred to as a Portable Wear Metals Analyzer, since it is predominantly used by the military to determine metals in lubricating oils of military vehicles and aircraft. The system exists as a two unit assembly, each unit weighing less than 18kg, and being about the size of a small suitcase. The instrument is capable of analyzing, with sensitivities to 1 ppm (in lubricating oil), iron, silver, chromium, copper, magnesium, nickel, silicon, and titanium. Upper limits of the linear dynamic ranges vary from 10-80 ppm, depending on the metal. Thus, the system would be useful for determining one of the four target inorganic species. However, the sensitivity appears inadequate for the determination of copper at the concern level in water, and determination in soil would require additional sample processing. In addition, it requires the provision of external electrical power.

A portable "field" system, the Model AAZ-2 AA spectrophotometer, is manufactured by Scintrex. The AAZ-2 system uses a tungsten filament to vaporize atoms from the sample and Zeeman modulation to correct for background. The system consumes only 500 watts of 110 V electrical power, due to the use of the tungsten filament rather than a heated graphite tube, and weighs 26 Kg. Argon gas is used for system cooling and flushing, although the consumption rate is sufficiently low that a 20 kg cylinder should last for a week of routine operation. The AAZ-2 is a microprocessor-based instrument that has most of the capability of laboratory-based AA systems. The base price of the unit is $20,000; an automated sample changer that holds up to 48 six mL samples is available for approximately $7,000. Reported limits of detection for copper and lead are 4 and 8 picograms in a 10 μL sample, respectively. This translates to 0.4 and 0.8 μg per liter, considerably lower than the targeted concern levels for aqueous systems reported in Table 1. Changing of the hollow cathode lamps is required for each element of interest. However, the entire procedure, including optical realignment, is supposed to require less than five minutes. This suggests that such a system could be used for the determination of all of the target elements. Another "portable" AA system is marketed by Buck Scientific. However, it is a flame based unit, which requires the supply of flammable gas in the field, and appears insufficiently rugged for field use. Of course, the same concerns about the safety of open flames would be applied to this instrument as well.

For the outfitting of a mobile laboratory, there exists a wide variety of small commercial AA systems. However, power consumption of and environmental support for (cooling water, exhaust removal, air conditioning) these systems is considerably greater than that of the Scintrex unit, and they offer essentially no improvement in sensitivity or ease of operation over the lighter weight system.

Recommendations

Atomic absorption is a relatively well accepted and very sensitive technique for trace element analyses. Like most other approaches, the method requires sample digestion before measurement. Since small systems that use low levels of electrical power are available commercially, it seems likely that an atomic absorption system would be a highly appropriate technique for the field determination of the target constituents. For example, it appears that the Scintrex AA system would be suitable for the final analytical determination of all four of the target elements, if the time require for lamp changing was not excessive.

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INDUCTIVELY COUPLED PLASMA METHODS

Background

Inductively coupled plasma emission spectroscopy (ICP), is the workhorse of today's analytical chemistry laboratory. About 70 trace elements can be determined with precision and sensitivity equal to or better than flame atomic absorption spectrometry. Nearly all metals can be determined in a range of about 0.01 to 50 nanograms per milliliter; the elements of Table 1 fall in the range of 1 to 10 ng/mL.

An ICP instrument consists of an ICP source into which a liquid containing the metal ions to be measured is introduced, a monochromator and/or polychromator, a photomultiplier light detector, and electronics to measure the photomultiplier signal and control the instrument. The ICP source consists of a quartz torch through which argon gas flows and into which the liquid sample, as fine droplets, is fed. The sample is broken into a fine aerosol by a device called a nebulizer. A radio frequency power source drives an induction coil that surrounds the torch at a frequency of about 30 MHz and a power of about 2 kW. After ionization in the argon is initiated, the gas in the torch will flow through the torch as a plasma at temperatures of 5000 to 10000°C. Nearly all components of the gas are converted to atomic species that emit light at wavelengths that are characteristic of the elements.

The monochromator or polychromator components of the ICP are the optical components that consists of an entrance slit through which light from the source enters, a diffraction grating system to disperse the light through an arc as a function of its wavelength, and one or more exit slits through which light exits to the photomultiplier(s). Monochromator instruments permit quantitative analysis of any one or number of elements by turning the diffraction grating to scan through the emission spectrum of the elements in the sample. Such instruments are normally used in research and non-routine analysis problems. In instruments with polychromators, multiple elements are determined by diffracting light through a number of exit slits each with its own photomultiplier. Thus, as many as 60-70 spectral lines, and as many elements, can be measured simultaneously. At a rate of measurement of one sample per minute, over two thousand elements can be measured per hour. Special filters can be used to make the exit slits highly specific for extremely narrow bands of light. Some polychromator instruments have a scanning accessory that permits each light exit slit to be scanned to a limited extent around the wavelength that is measured by the slit and provides a measurement of background on each side of the peaks of interest.

Approach and Evaluation

A number of these systems are commercially available. However, their utility for field analysis is limited because of their size, the need for exact alignment of their optical systems (in cases where simultaneous multielement determinations are appropriate), and utility

support requirements. For example, many of the systems occupy more than 30 cubic feet, weigh more than 400 Kg, and require both 220 volt and 110 volt power supplies, along with cooling water. Such a system could be supported only by the largest mobile van, or a stationary structure. In addition, plasma spectrometers still require that the sample be digested prior to analysis.

Recommendations

Although development is toward smaller and highly automated ICP systems, no instruments are apparently available at the present time that would be suitable for field use. It is unlikely that the required precision of optical alignment could be maintained in a mobile system. Also, the inherent strength of ICP (simultaneous multielement determination) is not used to its greatest advantage when the number of target species is relatively limited.

ELECTROCHEMICAL METHODS

Introduction

Electrochemical methods have been used for a number of years for the determination of metallic species in a wide variety of samples. The technology is relatively straightforward, from both an instrumental and manipulatory standpoint. A number of portable systems exist which could potentially be of use in a field scenario. The two electrochemical technologies which are most applicable to the determination of the target inorganic species are ion selective electrodes (ISE) and anodic stripping voltammetry (ASV). These are discussed below.

Approach and Evaluation

ISE's are usually fabricated from glass or some other solid material which has been doped with one or more ions of specific elements. The doping makes the electrode respond to one particular type or group of ions in solution. The potential across the glass membrane is determined by the ratio between the analyte ion in the solution being tested and the ionic species in the glass. ISE's have the advantage of a high degree of simplicity: that is, often the electrode is merely placed into a solution of the medium being tested, and the potential established across the glass membrane, which is proportional to the species being analyzed, is read. However, there are a number of drawbacks to their use. First, if information is desired about the total amount of a particular element present in a given sample, as opposed to the amount of a specific ionic form of that element (eg. total copper vs. Cu^{+2}), then this sample must undergo some form of chemical processing to convert all forms of the element in question into the particular species to which the ISE responds. This can often be a problem in natural water systems, where a large number of natural complexing agents can be present. For soil samples, the processing may be as rigorous as that which is required for other analytical methods, such as atomic absorption. Secondly, the number of interferences in a natural material can be large. Many ISE's respond to more than one elemental species. In a matrix of unknown composition, the use of an ISE would largely amount to a screening test. Obtaining a positive response would mandate the use of a more specific and sophisticated analysis in order to verify and quantitate the amount of the target species present.

Orion corporation markets a number of portable millivolt instruments, designed for field use with ion selective electrodes. In addition, Orion sells ISE's which are specific for copper and lead. The copper electrode responds to Cu^{+2} over a dynamic range of 0.64 μg/L to 6.4 g/L in water. Sensitivity for soil samples would depend on sample size. However, divalent mercury, a species likely to be present in the same matrices as those being analyzed for copper, and large amounts of divalent iron, interfere. The lead specific electrode is sensitive over a range of 210 μg/L to 20.7 g/L. Thus, some concentration of the

analyte would be required to reach the concern levels for aqueous samples listed in Table 1. Also, divalent forms of copper and mercury interfere. Therefore, it seems apparent that commercially available ISE's for copper and mercury will be useful only in those instances where previous remedial investigations have indicated that only single element contamination.

Anodic stripping voltammetry is potentially a very sensitive technique, since it acts to concentrate the species of interest in the electrode material prior to analysis. Briefly, a mercury drop or solid material electrode is placed in contact with the solution of interest. A large cathodic reduction potential is applied for a fixed length of time, in order to reduce the metallic ions present in solution and plate them in/onto the surface of the electrode. Given a sufficiently large amount of solution, the amount of material deposited is proportional to the duration of the applied potential. The potential is then switched and varied in an anodic direction, so as to oxidize the deposited metals out of the electrode. Typically, each metal is oxidized at a characteristic potential, such that peaks present at a particular potential are usually due to a specific metal. For unattended monitoring of natural water systems, ASV has the advantage of instrumental simplicity (although the power requirements are such that AC power must be supplied) and programmed operation. Of course, various strong complexing agents in the water sampled may tend to reduce the apparent amount of element present. Typically, anodic stripping voltammetry can attain sensitivities of 50 μg/L for copper and lead, which with a longer application of reducing potential for lead, would achieve the stated concern levels for these two species. Arsenic does not amalgamate with mercury (the typical electrode material), and mercury itself would have to be determined using an electrode made of another material, such as platinum or glassy carbon. Limits of detection for these species are on the order 10-20 μg/L for aqueous samples, mandating significant concentrating to attain the concern levels listed in Table 1.

Recommendations

Some electrochemical methods offer the advantages of simplicity and speed for the determination of some of the target species. ISE's for copper and lead are commercially available and are easily portable for use in the field. However, only the copper ISE is sufficiently sensitive to attain the concern levels, and it is subject to interferences from mercury, a contaminant which is expected to be present in the same samples. Anodic stripping voltammetry (ASV) offers the ability to determine all of the target species, albeit with two different electrode systems. However, commercially available ASV systems require AC power, and reaching the target concern levels would require greater than normal cathodic deposition times. Because of the potential interferences in natural systems (soil and water samples), ASV has equivalency with more specific methods such as AA, for some, but not all of the target analytes. Thus, it is recommended that electrochemical measurements be considered for field use only as screening tools, with positive results being followed by the use of more specific analytical methods.

X-RAY FLUORESCENCE

Background

When a chemical element is bombarded with photons (x- or gamma rays) that have energies higher than the binding energies (absorption edge energies) of the electrons in the atoms, electrons in some of the atoms are removed and vacancies in the electronic shells of the atoms are created. The vacancies are subsequently filled by electrons from the outer shells, and x-rays that are characteristic of the element are emitted. The energies of the x-rays are equal to the difference in the binding energies of the shells. This process of electron removal is called the photoelectric effect, and the overall process of excitation and subsequent x-ray emission is termed x-ray fluorescence (XRF). This process began to gain wide acceptance about 30 years ago as the basis of methods of elemental analysis and is now used in most well-equipped analytical laboratories. There are many thorough and excellent publications that describe this analytical method (1-4). An effect known as Auger electron emission competes with x-ray emission in the process of filling the electron vacancy. Because the Auger process predominates for elements of low atomic number, the energies of x-rays from the low "z" elements are so low that they are difficult to measure, and the characteristic x-rays have energies that are similar and difficult to resolve, analysis of elements below aluminum with XRF is not as useful as for the heavier elements.

Trace element analyses based on XRF generally employ semiconductor silicon or germanium detectors to count the emitted x-rays. The energies of the characteristic x-rays are resolved "dispersed" by the detector and the method is called energy-dispersive x-ray fluorescence analysis (EDXRF). Jenkins et al (2) state that both silicon and germanium detectors are able to resolve the Ka x-rays of adjacent elements for atomic numbers above 10. The energy resolution of the silicon detector is optimum in the energy range of 1-40 KeV, whereas, the germanium detector is better suited to energies above 40 KeV. Another technique referred to as wave-length dispersion makes use of crystal diffraction to spatially resolve the emitted x-rays. Wave-length dispersive systems were in use long before the semiconductor detectors and generally have better resolution. However, the energy dispersive method has adequate resolution for many analyses of interest and is much faster than the wavelength dispersive method because all of the emitted x-rays are measured in the same time period and a much larger fraction of the x-rays emitted from the sample are measured. Complete x-ray energy spectra can be rapidly acquired with the semiconductor detectors and stored in computer based multichannel analyzers. The spectra can then be reduced with computer programs that have been written to correct for the various types of matrix effects that perturb the results of trace element analyses. It should be noted that matrix effects in the sample are very complex and require considerable sophistication on the part of the computer program to prevent biases in the analyses. Matrix effects include attenuation of the incident beam of excitation radiation, fluorescence of one element

from the fluorescent radiation of another, attenuation of the fluorescent radiation from the element of interest, and various subtle combinations of these processes. The reader is referred to the work by Jenkins et al for a discussion of matrix effects in XRF (2).

The source of x-rays used to excite the sample can be either an x-ray tube or a radioisotope, but most laboratory instruments make use of x-ray tubes to provide an intense source of x-rays and the highest analysis sensitivity. The broad band of x-ray energies that come directly from x-ray tubes can be used to produce fluorescence in the sample. However, the background is relatively high when the broadband excitation is employed. A procedure that is used to decrease background and make analyses more sensitive and specific is the use of a secondary target which will yield x-rays of a specific energy that is then used to excite very efficiently a limited group of elements in the sample. Radioisotope sources are available with x-ray and gamma ray energies that can be used to efficiently excite x-ray fluorescence from all elements. A secondary target can also be used with radioisotope sources to produce a desirable x-ray energy for excitation. The use of secondary targets and filters as well as combinations of filters to improve the ability of XRF systems to measure trace elements is a vast subject that is discussed well by Jenkins et al (2).

Approach and Evaluation

Under the appropriate conditions and with state-of-the-art laboratory equipment, elements with an atomic number above Al can be detected with XRF down to concentrations of about 10 parts per million (ppm). With portable equipment presently available it appears that reliable measurements can only be obtained at levels of about 50-100 ppm or higher. In many cases, this degree of sensitivity can be achieved without chemical treatment of the sample. Recently, XRF has been studied to determine its capability for the analysis of soils for the toxic elements of interest in this assessment (5). These studies show considerable promise. Other investigations have indicated that the sensitivity of XRF can be extended sufficiently to measure nanogram quantities of elements if chemical separation procedures are employed to isolate and concentrate the elements of interest before the x-ray analysis is carried out (6). The analysis of water by XRF can be carried out directly if the trace element concentrations are high enough. If the levels are too low for direct analysis, simple chemical separation procedures can again be used to isolate and concentrate the elements to be measured.

Portable XRF systems that measure percentage level concentrations of trace elements in nearly any material have existed for many years (2). Only during the last few years with the advent of solid state microprocessors and/or portable computers has it been possible to bring some of the power of laboratory systems to portable units. At least two, and perhaps several more, portable x-ray fluorescence systems capable of trace element analysis at the ppm level either have been developed for commercial applications or are nearing such development.

One system, the Model 840 portable x-ray analyzer manufactured by Columbia Scientific Industries (CSI), has been used for waste site evaluation (5). This system is an energy dispersion instrument that makes use of radioisotopes to excite x-ray fluorescence, and a microprocessor-based, multi-channel analyzer (MCA) to count x-rays emitted by the sample and analyze the resulting spectrum. The instrument has interchangeable heads that contain different radioisotopes ^{55}Fe, ^{109}Cd, ^{241}Am, and ^{244}Cm to permit optimum analysis of different sets of elements. One head can be placed directly against the ground, a tree, etc., for a totally non-destructive, rapid-scanning analysis. However, as in most sampling problems in science, the most accurate and precise measurement is attained if homogeneous (dry, powdered soil sample) is measured. Heads are provided for this purpose. The system is powered by either 110 V AC or a 7.2 V DC rechargeable battery pack. Samples of precipitates and dust on filter paper can be measured thus allowing chemical isolation and concentration of elements before analysis. CSI claims that the system will measure all elements above titanium (element 22). Calibration of the Model 840 can be done on-site using soil samples containing known concentrations of the elements of interest as well as known levels of elements that might cause matrix effects that would bias the analysis. The microprocessor has a built-in calibration routine and can store calibration constants for eight types of samples. Information supplied by the manufacturer indicates that the instrumental limits of detection (LOD) are considered to be three times the so-called "counting statistic". This translates to LOD's of 93, 69, and 78 $\mu g/g$ soil for arsenic, copper, and lead, respectively. Detection limits for mercury are considerably higher, probably on the order of 1000 $\mu g/g$ soil, according to the manufacturer. The analyzer weighs approximately 20 pounds. The present base system price is approximately $50,000. The 840 system uses a gas proportional counter rather than a semiconductor detector, to measure x-ray intensity. Chappel et al (5) state that the resolution (FWHM) of the Model 840 is 0.83 keV or 14% for the 5.9 keV Ka peak of manganese (decay product of ^{55}Fe). Since current state-of-the-art silicon x-ray detectors have resolutions of slightly better than 0.15 keV for the Mn x-ray, it is obvious that the Model 840 could be significantly improved with a high resolution semiconductor detector.

Another portable XRF system which appears suitable for use is the ASOMA Instruments Model 8620 system. It is a small (45 cm x 28 cm x 18 cm, 8 kg), bench-top model analyzer, which has as an option, a battery pack, capable of powering the instrument for 8 hours between chargings. Thus, it can be considered as being truly portable. It possesses many of the same features as the CSI Model 840, including simultaneous multielement determination (6). Discussions with the manufacturer indicate that the instrumental LOD for CU is about 20 ppm ($\mu g/g$) in soil, at a precision of 20 - 30%, relative. Specification of the LOD's for AS, PB, and HG is more complicated. If resolution of the three elements is not required, then optical filters can be removed, and the LOD for all three elements combined is 25 ppm, with the same $\pm$20 - 30% relative precision. If discrimination among each of the three elements

is required, filters must be in place, which reduces the photon flux to the counting tube, which in turn reduces the sensitivity to between 100-200 ppm. The cost of the instrument is about $22,000, considerably less than that of CSI Model 840.

A third instrument which appears to possess comparable sensitivity and the capability of being operated as a portable unit is the Oxford Analytical Lab-X 1000 Series XRF systems. The unit weighs 41 lbs, and is designed to operate from line voltage. However, its power consumption is sufficiently low that it could be operated from a 30 lb battery pack/inverter system which would provide enough power for 5 hours of continuous operation (although this would comprise a development activity and take it out of the realm of strict commercial availability). The sensitivity of this unit appears comparable to the Columbia Scientific portable system, with LOD's in the range of 50-100 ppm in soil for most elements (probably closer to 200 ppm for mercury). However, it possesses two advantages which make it an attractive alternative to the other portable units. First, its cost is about $15,000, considerably less than that of the other units. More importantly, it is equipped with a 256 channel multi-channel analyzer, the output of which can be viewed directly by the operator. This means that the operator can see an x-ray spectrum of the sample while its being taken. This enables the operator to make a qualitative decision as to what interferences might be present in the wavelength region of the target elements.

As this document was going to press, HNU Systems, Inc., was announcing that it would soon market a portable XRF system. As portrayed in its initial literature, the system fits on to a small dolly cart, or hand truck. Thus, while it is powered by a rechargeable battery pack, it may be considered more mobile than portable. However, the manufacturer does offer an optional backpack for the device. The system uses radioactive sources, similar to those in use on other portable systems. However, the HNU system uses a lithium drifted - silicon detector with a multi-channel analyzer, affording improved resolution over more conventional proportional counters. Company representatives indicated that they are currently seeking input from the potential user community on ways of making the system more portable. Thus, it appears that this system is not yet in its final configuration. Tentative price for the system is $40,000.

Note that there are other portable XRF systems on the market (see Appendix B). However, they are primarily designed for determination of the metal content of bulk materials, such as ingots, steel beams, etc., and lack the sensitivity to be of significant use for analysis of environmental samples.

Another portable system that currently exists in the prototype stage has been fabricated by Martin Marietta at their Colorado Aerospace Center. This system appears to have much of the sophistication of a laboratory instrument, as much of the system components were developed for the NASA Mars Viking Lander program. The instrument is an energy

dispersive system that uses a high resolution silicon detector, and a small conventional 1024 channel analyzer to acquire spectra. A Gridcase 2 lap-top computer is used to analyze the x-ray spectra. The excitation source is a 30 kV x-ray tube. This voltage is too low to permit the use of a secondary target whose x-rays would excite the K x-rays of cadmium; secondary targets could be used to measure Cu, Cr, and As by their K x-rays. Like the CSI system, this instrument can be placed directly on the ground for rapid scanning for highly elevated levels of toxic elements. The system has been preliminarily evaluated by EPA for soil analysis; initial results are highly encouraging (7). Information provided to us by one of the development engineers suggest that LOD's for soil samples are about 150, 250, 70, and 80 $\mu g/g$ for AS, CU, PB, and HG, respectively. For water samples, LOD's appear to be approximately 20, 75, 30, and 50 ppm, or mg/L. Thus, from purely a sensitivity standpoint, it would appear that this prototype system would not offer substantial advantages over the CSI Model 840 system, with the exception of the determination of mercury. For mercury, it would have substantial advantages in sensitivity, because of the very high LOD for HG with the Model 840. No estimated value for what the cost of the system would be if, and when, it is made commercially available.

Another approach for trace element measurements at remote sites would be a full-scale laboratory XRF system. This is the approach being employed by NUS Corporation, in support of EPA activities in the Northeastern U.S. (8). There are many suitable units manufactured by such companies as EG & G Ortec, Tracor X-Ray (a Division of Tracor Northern), Kevex, etc. One typical, advanced system is the Kevex Delta XRF Analyst. This EDXRF instrument is a sophisticated computer controlled system with a 60 kilovolt x-ray tube that will operate at up to 200 watts. Totally automated and under computer control are the tube voltage and current, sample changing, and the selection of one of six secondary targets for optimizing the measurement sensitivity for all elements. The maximum tube voltage is sufficient to use a secondary target that will excite the K x-rays for elements up to element 63 (Erbium). While it is difficult to obtain specific LOD's for the target elements for such systems from the manufacturers, crude extrapolations from data concerning geologic samples suggest that they should be on the order of a few ten's of $\mu g/g$ soil. Cost of the Kevex instrument would be approximately $100,000 or about twice the cost of the most sensitive portable units. Unfortunately, the size and power requirements for such systems appear to make them impractical for a field setting, unless they are placed in a mobile van. However, these systems do offer the advantages of somewhat greater sensitivity and selectivity than the portable units, while limiting sample work-up to physical manipulation.

Recommendations

Neither the portable nor the more sophisticated laboratory units are capable of analyzing all the target species at or below the concern levels stated in Table 1 without some prior sample manipulation or concentration. However, the truly portable CSI Model 840 offers a potentially powerful tool for rapid determinations for the target species in highly contaminated areas. For example, portable XRF could be used in the initial stages of monitoring the restoration of an area, substantially reducing the analytical work load during this period. Then, as levels of the target species drop below the LOD's for the system with continuing clean-up of the area, more conventional analytical systems or approaches, such as AA or colorimetric analysis, could be employed. The ASOMA Model 8640's capabilities are somewhat less than that of the CSI's. However, the claimed higher sensitivity of the ASOMA model for the combination of AS, HG, and PB offers some interesting possibilities for screening approaches. For example, the ASOMA instrument could be used as a 25 ppm screening tool in remedial action situations. Any area determined to be higher would be considered to be contaminated. Any area registering lower than the 25 ppm level would be subject to additional analyses. The Oxford Analytical system, while not strictly portable, could be easily made so, has comparable sensitivities, and offers both cost advantages, and the capability of viewing the x-ray spectrum as it is generated.

The use of coprecipitation of the target elements, followed by filtration on to a relatively small area as a means of concentration (see section on sample processing) appears promising for the extension of the limits of detection of portable XRF. In such a scenario, samples which register at or below their LOD's could be microwave digested and processed appropriately. This would effectively extend the LOD's by several orders of magnitude. It is likely that some developmental effort would be required to insure compatibility of the filtration area with the geometry of the XRF sensor head.

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SUMMARY RECOMMENDATIONS FOR INORGANIC SPECIES

Establishing recommendations for appropriate field analytical technology for both remedial investigations and actions is a complex task, because of the competing needs of the two activities. Where remedial investigations are concerned, direct knowledge of the contaminants present is often limited. Thus, it is probably more appropriate to focus on those techniques which provide as much information as possible on a given sample. Such an approach would tend to favor multi-component techniques, such as ICP, or GC/MS. In addition, the need for very rapid turnaround time may not be as critical as for the remedial action situation, in which restoration crews may be placed on standby awaiting the outcome of analytical determinations. Thus, in the remedial investigation phase of a project, off-site analysis of collected samples may be a more cost effective approach. This situation is in contrast to that of remedial action, where the nature of the contaminants and their approximate magnitudes are usually known. Target constituents are typically defined, as are the levels of concern for each species. Turnaround time would seem even more important, as the level of a given contaminant in a particular sample will often be used to guide the next restoration activity. Ideally, turnaround time should be limited to a matter of minutes. However, in a remedial action situation, accuracy and precision may not be as important, since, usually for legal purposes, a final, laboratory based analysis would likely be performed on a given parcel of land or water prior to declaring that the contamination had been removed. The recommendations given below should be taken given these considerations. In this case, while the approaches described below certainly can be employed for remedial investigation, more weight has be given to those approaches which seem most appropriate for remedial action situations.

In the strictest sense, the term "portable" refers to those approaches and instrumentation which can be hand carried and used in the field without external power or vehicle support. Given this strict interpretation, with the exception of the use of portable XRF instrumentation for the determination of copper in soil, no commercially available technology is capable of determining all of the target species in soil and water at the concern levels stated in Table 1 without extensive sample preparation. The Perkin-Elmer Portable Wear Metal Analyzer, which contains an integral sample digestion unit and is highly ruggedized for rapid transport from location to location, will determine copper over a range of 1-20 ppm in soil samples (and would probably do so in water samples), but its utility for soil samples appears to be limited. In addition, while its name implies portability, it, in fact requires the supply of external electrical power. For portable sample processing, instrumental options appear to be limited to a hot plate heated with a gasoline or propane fueled camp stove. In such situations, concerns may be raised about the safety of open flames in continual use. The solid phase Geoflux appears promising for low temperature digestion of soil samples, primarily because no liquid acids are employed, and the heating period over a

propane flame should be five minutes or less. The use of such material would require some development effort. In terms of species analysis, commercially available colorimetric test kits could be used for copper (below the detection limit of XRF) and lead. Mercury (below the limit of detection for XRF) could be analyzed using cold vapor generation, with a portable gold foil amalgamation detector. Arsenic would be determined using arsine generation, followed by colorimetric detector tube or portable instrumental determination. Such an overall approach is likely to be the most straightforward of all those considered, for the following reasons. The sample processing steps are well documented in the literature, the colorimetric tests are simple and easy to conduct, and the portable arsine and mercury monitors should be straightforward to operate. However, there are sufficient limitations and difficulties with such approaches so as to recommend them only when there are no other options. First, hot plate sample digestion in the field is tedious, very labor intensive, and potentially dangerous, since it requires handling large amounts of acids in a non-laboratory environment and would require open flames. In addition, it requires large amounts of time. From an analytical standpoint, while negative results from the colorimetric tests would be quite meaningful, the large number of interferences in matrices as complex as soil and water are likely to generate an unacceptably large number of false positives.

We believe that a more appropriate approach is the use of what can be referred to as fieldable instrumentation or analytical systems. Such instruments might be too bulky or heavy to be hand carried, but would be sufficiently rugged to be moved in the bed of a pick-up truck. Such a designation would also include those systems which require some external electrical power which could be supplied by a reasonably small gasoline powered generator or inverter system driven off an automobile engine. If such an approach were taken, it would open a number of options which would make field analysis of the target species a practical reality. In terms of sample processing, the use of microwave aided digestion of soil and water samples would reduce the time and effort required so as to make in-field digestion both practical and safe. Effort would be required to establish the exact times and power settings for digestion of the matrices of interest. An alternative to the use of microwave digestion may be the use of low temperature dry fluxes. Again, effort would be required to determine the exact conditions under which thorough sample digestion would be achieved. However, while the digestion would require the intermittent use of an open flame (small propane torch), no external power would be required.

The availability of power through the use of a small generator would permit the use of a small atomic absorption spectrophotometer. While theoretically it would be possible to determine all of the target elements by AA, this would require considerable changing of lamps and subsequent warm-up time, and therefore, might not be practical on a routine basis in the field. However, this can only be determined by evaluation in the field. It may be more practical to rely on arsine generation and mercury vapor generation, followed by analysis using portable instrumental monitors, for the determination of arsenic and

mercury, respectively. If arsenic can be determined in a timely manner using the same small field AA instrument used for copper and lead analysis, then the employment of a separate arsine generation/analysis system would be obviated. Portable XRF instrumentation could be of use for samples which are contaminated below the existing instrumental detection limits if digestion followed by some additional sample concentration were employed. The additional steps would probably be limited to pH adjustment and coprecipitation. Some development effort would be required to establish procedures for depositing the small amount of precipitate on the filter in such a configuration so as to be compatible with the geometry of the sensor head on the XRF unit.

The outfitting of a mobile laboratory with full scale laboratory instrumentation, such as an ICP spectrophotometer, is not recommended at this time. It appears that the development time and effort required to integrate two large systems would not be justified, since it is likely that a mobile lab would not provide data of substantially higher quality or at greater speed.

From these recommendations, the following field strategy seems to evolve. Portable XRF is recommended for first use as a screening system for soils, especially in those areas which are suspected of heavy contamination. This should reduce the analytical burden considerably for those areas in which contamination is high, because portable XRF analysis requires the least amount of effort. Choice of the specific instrument depends on the specific application. The CSI X-Met 840 appears to have lower limits of detection than the ASOMA Model 8620 for CU, PB, and AS, taken individually. However, the ASOMA unit is claimed to have superior sensitivity for AS, PB, and HG, taken together. If XRF is to be used solely as a screening device, then the ASOMA unit may be more useful, as the "trigger" level for AS, PB, and HG would be at least a factor of 3 lower. If, however, there is need to determine in the field the individual element which is above the concern level prior to further analysis, then the CSI unit would be the instrument of choice. Recall that neither of the units is likely to be able to detect HG, AS, and PB at the concern levels stated in Table 1 in the background section of this report. Concurrent with the use of XRF, some effort should be placed into investigation of the utility of the micro-coprecipitation approach for extending the limits of detection below about 80 ppm. Once a matrix is analyzed which has levels below those of the LOD for XRF, samples could be digested in a microwave system (CEM Model MDS-81D) or digested with a low temperature flux, and colorimetric test kits for copper and lead should be employed as screening tools. If results from the test kits are positive for copper or lead, the small Scintrex fieldable AA system would be used to confirm the results and provide quantitative data. (If arsenic can be determined expeditiously with the same AA system, then it too would be determined at this point in the analysis scheme. This would be determined during a laboratory evaluation of the Scintrex instrument). For arsenic and mercury determinations, the volatile species generation, followed by quantitation using portable instrumental monitors (Jerome Instruments Model 411 Mercury Monitor and Sensidyne

Model SS4000 Arsine monitor are recommended) is the procedure of choice. This tiered approach has the advantage of only committing to the more labor intensive and time consuming methods after the more rapid screening methods have indicated the need to go further.

ORGANIC SPECIES: INTRODUCTION AND SAMPLE PROCESSING

The target organic compounds are listed in Table 2. These consist of the highest priority ("primary") target compounds and other ("secondary") compounds which are typically present in areas contaminated with the primary target compounds. Important physical properties for the primary compounds are listed in Appendix A. The secondary compounds were compiled from those found by Ebasco Services Inc. (1) in samples from the Rocky Mountain Arsenal site. The latter are included because they represent additional toxic compounds which may be important to measure and they also are sample matrix components which may present interferences to the determination of the highest priority organic constituents. From a physical property and analytical standpoint, the target organic compounds are divided into volatile and semivolatile constituents. The division between the two is a boiling point (at 760 mm Hg) of ca. 150°C. Within each division, the chemical types of the target compounds are classified as aromatic, halogenated, olefin, pesticide and intermediate, and miscellaneous. As is the usual practice in laboratory-based analyses, each type requires a somewhat different analytical approach and different instrumentation for determination in the field. Both sample preparation and analysis must be considered. Thus, it seems practical to consider the analyses as volatiles, semivolatiles, and pesticides, as is done in the EPA Contract Laboratory Program (CLP). Methods suggested for the pesticide target analytes should be applicable to all pesticides on the Hazardous Substance List used in the CLP. Similarly, volatiles and semivolatiles can be considered in a generic fashion.

In virtually all trace organic analyses, some form of sample preparation and/or concentration is used. The type of sample preparation depends on: (1) the nature of the analytes; (2) the matrix to be prepared; (3) the ultimate detection limit required; and (4) the expected interferences. For the purposes of this technology assessment, the additional factors of turnaround time and fieldability must be considered as well. There are essentially two classes of analytes, the "volatiles" and the "semivolatiles". These are distinguished more according to the appropriate sample preparation scheme than to volatility per se. There are three possible matrices: air, water, and soil. The action levels for these compounds are listed in Table 1 and represent a challenge even for currently used laboratory methods. This challenge mandates comparison of the merits and deficiencies of the various sample preparation options.

For samples containing volatile organic compounds, adsorption/thermal desorption is the only sample preparation technique capable of operation on all sample matrices. This technique should be appropriate for benzene, trichloroethylene, DIMP, and possibly dibromochloropropane and dicyclopentadiene, as well as other high volatility species. For air samples, either above ground or soil gas, a known volume of the air would be drawn through a sorbent tube (probably Tenax-GC or other adsorptive resin). The tube would then be inserted into an analytical instrument for desorption and quantitative analysis. This would be a

Table 2. Primary and secondary target compounds

Volatile organic compounds						
Priority	Chemical class	Compound	Boiling point, °C	Vapor pressure, Torr @ 20°C	Water solubility, mg/L @ °C	Ionization potential*, eV
Primary	Aromatic	Benzene	80	75	1,780 @ 20	9.25
	Halogenated	Trichloroethylene	87	60	1,100	9.45
		Tetrachloroethylene	121	14	150 @ 25	9.32
Secondary	Halogenated	Methylene chloride	40	-	-	11.35
		Chloroform	61	-	-	11.28
		1,2-Dichloroethane	83	-	-	11.06
		1,1,1-Trichloroethane	74-76	-	-	11.25
		1,1,2-Trichloroethane	110-115	-	-	-
		1,1,1,2-Tetrachloroethane	138	-	-	-
		1,1,2,2-Tetrachloroethane	147	-	-	-
	Aromatic	Ethylbenzene	136	-	-	8.76
		m-xylene	138-139	-	-	8.56
		o-xylene	143-145	-	-	8.56
		p-xylene	138	-	-	8.45
		Toluene	111	-	-	8.82
	Misc.	Bicycloheptadiene	89	-	-	-
		Methyl acetate	57.5	-	-	10.27
		Dimethylsulfide	38	-	-	8.69
		Methylisobutyl ketone	114-116	-	-	9.30

Table 2. Primary and secondary target compounds (Cont'd)

Semivolatile organic compounds							
Priority	Chemical class	Compound	Boiling point, °C	Melting point, °C	Ionization potential, eV	Vapor pressure, Torr @ °C	Water solubility, mg/L
Primary	Olefin	Dicyclopentadiene	170-172	-	7.74	10 @ 48	-
	Halogen.	1,2-Dibromo-3-chloropropane	196	-	ca. 10.4**	0.8 @ 21	1,000
	Phosphon.	Di-isopropylmethylphosphonate	69 @ 16 torr	-		2 @ 70	-
	Pesticide	Aldrin	-	104	-	7.5×10^{-5} @ 20	0.01
		Dieldrin	-	176-177	-	3.1×10^{-6} @ 20	0.1
		Endrin	-	245 (dec.)	-	2×10^{-7}	-
Secondary	Pesticide	Chlordane	-	-	-	-	-
	Intermed.	Isodrin	-	-	-	-	-
		pp'-DDE	-	88-90	-	-	-
		pp'-DDT	-	107-109	-	-	-
		Atrazine	-	-	-	-	-
		p-chlorophenylmethylsulfide	-	-	-	-	-
		p-chlorophenylmethylsulfone	-	-	-	-	-
		p-chlorophenylmethylsulfoxide	-	-	-	-	-
		Hexachlorocyclopentadiene	-	-	-	-	-
	Aromatic	Diethylbenzene (o,m,p)	180-182	-	-	-	-

*Source: Ionization potentials from Photovac Technical Bulletin No. 11, Photovac, Inc., New York, NY (1986).

**Estimated from structurally similar compounds.

simple and straightforward way of assessing the level of volatile organic contamination in a particular area, although the relationship between the soil gas concentration and the subsurface contamination would need to be established. For water and soil samples, the above compounds could be purged onto the trap containing adsorptive resin, which would then be analyzed as described above. The equipment required for this type of sample preparation would be a battery-operated sampling pump, a purging device, and the trap. This sample preparation technique is widely accepted for use in the laboratory, and results in the field would not be expected to differ substantially from those obtained in the laboratory. If identical procedures were used, preparation of the air samples would require only sufficient volume to meet the desired limit of detection, and preparation of the water and soil samples would require 5-10 minutes. From the standpoint of sample throughput, it is likely that the purge and trap sample preparation could proceed faster than the actual rate of chromatographic determination. An additional advantage is that the sample size can be easily adjusted to provide the degree of concentration necessary to meet the target detection limits. The sorbent tube design would conform to the injection port geometry of the measurement instrument.

Three other sample preparation techniques could be used for water and soil samples -- solvent microextraction, solid sorbent extraction, and heated headspace purging. The solvent microextraction and heated headspace methods are less sensitive than thermal desorption because only a fraction of the total sample is actually analyzed. However, these approaches might be adequate in some cases. The latter (heated headspace) is preferred for field use because of its greater simplicity and the elimination of solvents which would have to be carried into the field and returned to the laboratory for disposal. It also minimizes contamination of the chromatograph by less volatile sample components. The heated headspace option is discussed below.

The technology for recovery of volatile organic compounds from soil matrices by the static heated headspace technique utilizes EPA SW-846 Method 3810 (2). This method specifies heating 10 g of soil in a septum-capped 125 mL bottle at 90°C for 1 hr. A 2 mL aliquot of the headspace gas is injected into a GC. The only required equipment for sample preparation is a thermostated water bath or heating block and bottles with septum-lined screw caps. In the field, a water bath maintained on a camp stove may be sufficient. Of course, there would be the concerns regarding the safety of the continual use of open flames. The use of a propane stove may be mandated, since benzene, one of the target compounds, is frequently a component of the gasoline. It is possible that the addition of small amounts of highly saline water may improve recoveries and reproducibilities. Some further developmental work in optimizing the sample preparation for in-field use is likely to be required.

The sample preparation method for water has received more attention, and more definitive procedures are available. The suggested procedure (3) is similar to that noted above for soil. It utilizes 100 mL of

water in the same 125 mL septum-capped container. In this case, equilibration of the volatiles with the headspace is achieved in 1 minute of shaking. Addition of sodium chloride (to a 20% concentration) increases the equilibrium and response of halogenated hydrocarbons by ca. 2-fold, and heating the sample container to 39°C increases the responses by ca. 4 to 6-fold over 0°C. For field use, the heating and shaking should be sufficient. After the equilibration step, an aliquot of the soil or water container headspace is taken through the septum using a gas syringe and is directly injected into a GC. Calibration is achieved by the injection of headspace from blank samples of soil or water (e.g., sand or laboratory water previously demonstrated to be free of detectable volatile organic compounds) which have been spiked with known amounts of authentic standards. Recoveries also can be determined by spiking field samples. These operations can be conducted either in the field or in a laboratory prior to sending the instruments out into the field. As regards sensitivity, the SW-846 method for soils is designed (2) to achieve 1 μg/g. Precision and accuracy are not specified, but the method is recommended (2) for screening purposes only because of its variability. Considering the ability of a gas chromatograph's (GC) photoionization detector (PID) to detect pg masses of benzene or ppb concentrations of benzene in air (see Table 3), a 10-fold improvement in the limit of detection for soils should be possible. In contrast, the headspace method is quite good for water samples, and the results for chlorinated hydrocarbons using the electron capture detector (ECD) reportedly (3) are equivalent to those of the purge and trap method, while the sample throughput is approximately doubled (ca. 25/8 hour shift in a laboratory). Under very carefully controlled laboratory conditions, precision of ca. 3% can be achieved, while for routine analysis of numerous water samples a precision of 5 - 10% is more typical (3). In the field, the precision and sensitivity may not be as good as that attainable in the laboratory. These factors will depend largely upon the characteristics of the samples (degree of contamination by other organic compounds as well as suspended matter, concentrations of the target compounds, etc.) and the severity of the field conditions. The sensitivity of the method depends upon the compounds determined and the detector used, as well as the mass of water sample, headspace volume, and volume of headspace taken for GC analysis. Consideration of the reported sensitivities of the portable GC detectors and theoretical calculations (4) of the water/air distribution of many of the primary and secondary target compounds, a determination to 50 μg/L might be achieved, allowing a conservative 10-fold factor for the rigors of analyses in the field. This would not be adequate to attain the concern levels listed in Table 1, but the technique has potential for remedial investigation purposes.

Semivolatile Organic Compounds: At the current time, the best available commercial technology for preparing soil samples utilizes solvent extraction techniques. In laboratory-based analyses, soil samples are solvent extracted using either ultrasonication (as in EPA SW-846 method 3550) or the soxhlet apparatus (method 3540) (2). Neither of these methods is suitable for field use. The most feasible

Table 3. Comparison of total volatile organic compound survey meters

Manufacturer:	Photovac	HNU Systems, Inc.	Analytical Instrument Development, Inc.		
Instrument:	TIP I Total ionizables air analyzer	PI-101 Hazardous waste detector	590 Portable organic vapor meter/gas chromatograph	580 Portable organic vapor meter	710 Portable total hydrocarbon analyzer
Features					
Detector[a]	PID/11.7,10.6, 9.5, 8.4	PID/11.7,10.2, 9.5	PID	PID	FID
Response time,[c] sec/range	3[b]/10-90	3/0-90	2	2	5/90
Detection limit[c]/ compound[d]	0.05 ppm/Bz	0.2 ppm/Bz	0.1 ppm Bz - OVM 0.05 ppm Bz - GC	0.1 ppm Bz	0.1 ppm CH_4
Range; ppm	0-2000	0.2-2000			
Linear range, ppm	0-100, ±10%	0.2-500	to 2,000	to 2,000	1-2,000
Stability, % drift/hrs	100-1000, ±15%	1%/24 hr			
Precision 1% (10 ppm Bz)					
Field pack[e]	B	B	B, G	B	B, G
Battery charge, hrs	16	>10	8	8	8
Ambient conditions,					
Temperature, °C		to 40			
Relative humidity, %		to 95			
Dimensions, cm					
Probe, 2 xd	45 x 6.3	28.5 x 6.3	-		
Central unit, hxwxd	-	16.5 x 21 x 13	15.2 x 22.9 x 35.6	76 x 22.9 x 25.4	10.2 x 21.6 x 25.4
Mass, lbs/kg	3/1.5	8.4/3.8	15/6.8	8.2/3.7	14/6.4
Special features			Includes ambient temperature GC mode		Adjustable audio alarm
Price, $/T	3.3	3.3	6	3.9	4.5

[a]PID = photoionization detection/lamp eV.
[b]3 sec for 10% to 90% full scale detection to 10 ppm benzene.
[c]OVM = organic vapor monitor mode, GC = gas chromatographic mode.
[d]Bz = benzene.
[e]B = battery, G = compressed gas (specified, if listed).

Table 3. Comparison of total volatile organic compound survey meters (Cont'd)

Manufacturer:	Foxboro			Bacharach Instruments
Instrument:	OVA 128	OVA 108	OVA 88	TLV sniffer
Features				
Detector[a]	FID	FID	FID	Catalytic oxidation
Response time,[c] sec/range	2/90-OVM	6.2/90	<2	
Detection limit[c]/ compound[d]	0.2 ppm CH_4 - OVM "low ppb" CH_4 - GC	1 ppm CH_4		C_6H_4
Range; ppm	0.2-1,000 in 3% scales	1-10,100 log scale	1-100,000 log scale	0-10,000 in 3 scales
Linear range, ppm				
Stability, % drift/hrs				
Precision				
Field pack[e]	B, H_2	B, H_2	B, H_2	
Battery charge, hrs	8		>8	
Ambient conditions,				
Temperature, °C				
Relative humidity, %				
Dimensions, cm				
Probe, 2 xd	10 x 23 x 30	10 x 23 x 30	10 x 23 x 30	8 x 12.7 x 16.5
Mass, lbs/kg	12/5.5	12/5.5	11/5	5.5/2.5
Special features	Includes ambient temperature isothermal GC mode, adjustable audio alarm.	Similar to OVA 128 w/o GC. Less sensitive. Adjustable audio alarm.	Adjustable audio alarm	Adjustable audio alarm
Price, $/T	6	5		

[a]PID = photoionization detection/lamp eV.
[b]3 sec for 10% to 90% full scale detection to 10 ppm benzene.
[c]OVM = organic vapor monitor mode, GC = gas chromatographic mode.
[d]Bz = benzene.
[e]B = battery, G = compressed gas (specified, if listed).

method utilizes a hot solvent extraction by shaking, followed by a solid phase extraction (5). A 10 g aliquot of soil is shaken with 100 mL of methanol and heated briefly in a hot water bath. After shaking again, the bottle is allowed to cool while the soil settles in the solvent. A ca. 80 mL aliquot of the supernatant is diluted with a 2.5-fold volume of water and is passed through a 6 mL octadecylsilane bonded phase extraction column. The column is washed with one column volume of water and the target semivolatile compounds (except for diisopropylmethylphosphonate) would be eluted with 1.5 to 2 mL of hexane. Further purification (if needed) could be performed using a modification of EPA SW-846 method 3620 (2) by passing the hexane eluate (after brief drying over sodium sulfate) through a Florisil solid phase extraction column and eluting the target compounds with ethyl ether/hexane (15/85, v/v). Other solvent combinations also are possible. The diisopropylmethylphosphonate may require a more polar solid phase extraction media, such as a diol bonded phase column, and a stronger eluting solvent. Developmental work is needed to determine optimum conditions for recovery of this compound.

It is clear that such a protracted sample preparation scheme would be very unwieldy in a field scenario. There is, however, a quasi-soxhlet extractor known as the Soxtec, made by Tecator. This system uses heated solvent to extract soil samples contained in thimbles. The solvent is recycled and concentrated, and the sample is ready for injection into a GC. The technique has been reported (6,7) to be at least as effective as conventional soxhlet extraction. The advantages of the use of such a system include: (1) 20 minute extraction time versus 18 hours; (2) low solvent consumption; and (3) portability. This is the only device available capable of keeping pace with the gas chromatographic analysis of semivolatiles. The requirement for heating the solvent could be resolved as discussed earlier, using a propane burner and ethylene glycol as the heat transfer medium. Alternatively, the Soxtec could be run using electrical power supplied from a small generator or an invertor mounted in the vehicle carrying the Soxtec. The generator would be placed remotely from the area of sample preparation, in order to reduce noise exposure of the individuals working in the area and to reduce potential contamination of any samples with gasoline fumes.

An alternative to the exhaustive, quantitative extraction approach is the acceptance of less than quantitative recovery of the target analyte. For example, if consistent recoveries of 45% are adequate, then the field analysis may still be useful, especially if the field analysis is not be used for a final analysis with regulatory weight. The acceptance of low recoveries opens up a considerable number of possibilities for high speed, low labor intensity sample processing in the field. For example, merely shaking the soil or water sample with an appropriate organic solvent may be sufficient to recover half of the organic contaminants. This approach is currently being used for some field surveys in EPA's Region X (9).

Solid phase adsorbents are highly effective for recovering semivolatile organic compounds from water. Following a commercial method for pesticide recovery (8), 100 mL of water are passed through a 6 mL octyl bonded phase extraction column, 1 mL of pure water is used to wash the column, and the target compounds are eluted using 1.5 to 2 mL of hexane. Addition of a small volume of methanol or isopropanol to the water sample may be necessary to improve the wetting of the packing material by the sample. The eluate is analyzed by injection of aliquots into appropriately equipped GCs. As noted immediately above, the diisopropylmethylphosphonate may require different extraction conditions.

A technology capable of providing the performance of standard solvent extraction systems in the field is the use of the Mixxor device from Cole-Parmer. This device resembles a tissue homogenizer and relies on piston action to provide intimate contact between the solvent and water sample. As a result, a single extraction is sufficient for recovery of the analytes, and a minimal amount of solvent is required. In the most favorable of cases, a concentration factor of fifty can be achieved, as compared to a factor of one hundred using the laboratory technique. No evaporation of the solvent is required, and the extract can be injected directly into the measurement system. The unit is easily cleaned, and no further sample preparation is usually required. This is the recommended sample preparation technique for semivolatiles in water, regardless of whether a more sophisticated extraction system is available.

Recommendations

Because of its speed and simplicity, purge and trap technology is the method of choice for the isolation of volatile organic compounds from water and soil. For the extraction and concentration of semivolatile organics from water samples, the Mixxor system is probably the most straightforward system to use. However, solid sorbent sampling may also prove useful. For extraction of pesticides or other semivolatiles from solid samples, the time and labor required to perform a conventional extraction and clean-up mandate the use of a Soxtec liquid extractor for field use.

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SOIL GAS METHODS

Background

Soil gas sampling is a technique used to locate high concentrations of underground chemicals by detection of these chemicals in the soil gas. This technique may be used either to locate areas where the ground water is contaminated or as a method to assess soil contamination. This technique was first used in oil exploration to help locate underground deposits of gas and oil by the detection of chemical markers in the soil gas above the deposits (1). This technique has recently been applied to the detection of organic contamination of ground water (2-4). Volatile organic compounds (VOC's) lend themselves most readily to detection by this method, since they develop a significant vapor pressure over solutions of these compounds in water. The technique of soil gas measurement is strictly a sampling technique, since the analytical methods presently used to analyze soil gas samples have already been well characterized.

Swallow and Gschwend (5) have proposed a three-stage model for vertical transport of volatile compounds from contaminated ground waters. Gaseous diffusion is the method of transport in the unsaturated, or vadose, zone. Below this there exists a capillary fringe, where transport occurs both by transverse dispersion and by partitioning between the ground water and soil gas. The third zone, existing below the capillary fringe is the saturated zone. In the saturated zone, VOC transport occurs by transverse dispersion. In accordance with the proposed model of Swallow and Gschwend, there are three possible theories for the transport model of organic vapors in soil gas (6). In theory A, the rate determining step for vertical transport of VOC's is gaseous diffusion in the vadose zone. This theory would predict a finite concentration of VOC's in the soil gas, with the concentration varying linearly with soil depth. In theory B, the rate determining step for vertical transport of VOC's is dispersion in the saturated zone. For this theory, the soil gas concentration of VOC's would by very small, since the VOC's would diffuse from the soil faster than they were being supplied from the saturated zone. In theory C, the behavior would be intermediate between theory A and theory B. In cases where soil gas samples obtained over chemically contaminated ground water have been observed to contain measurable quantities of VOC's, either theory A or theory C appear to more accurately describe the method of VOC transport.

There are two general types of soil gas samplers for the detection of volatile organic compounds in contaminated ground water. These are active samplers and passive samplers. Active sampling systems typically utilize a probe which is driven into the soil to a predetermined depth. An air sample is pumped either through sampling ports in the end of the probe or directly from the sampling hole, collected in a gas-tight syringe or on a solid sorbent trap, and analyzed by gas chromatography on-site or off-site. Active sampling systems can allow the acquisition of near real-time information. This

means the sampling plan can be modified during the surveying process, thus permitting more efficient sample acquisition. This is balanced against the need for on-site analytical capability. Passive sampling systems utilize solid sorbent materials to trap volatile organic compounds. The passive samplers are buried underground and left for a period of time. The solid sorbent material traps organic compounds from the soil gas during this time. The passive sampler is then recovered and transported off-site for analysis. Data obtained from passive sampling is less drastically affected by short-term fluctuations in volatile organic compound concentration. Passive sampling also does not require on-site sampling capability. However, passive samplers typically require long exposure times and additional time is required for analysis time off-site.

Approach and Evaluation

The Lockheed gas analysis system (LGAS) active sampling system has been field tested for the measurement of chloroform, benzene, and chlorobenzene in the ground above ground water plumes known to contain large amounts of these three compounds (7). With the LGAS system, a probe was driven into the ground to the desired depth. A gas sampling manifold was attached to the end of the probe, and soil gas was drawn into the probe and gas sampling manifold by a manual air-sampling pump. Samples were withdrawn from the gas sampling manifold through a septum using gas-tight syringes. The contents of the syringe were analyzed on-site by gas chromatography. Soil gas sample data gave a linear correlation coefficient of 0.85 with ground water chloroform levels, giving a statistical significance of greater than 95% for six data points, but failed to detect benzene and chlorobenzene in the soil gas above ground water heavily contaminated with these two compounds. However, 90% significant correlation was found between carbon dioxide measurements made with a carbon dioxide detector tube (Draeger) on the soil gas above the benzene and chlorobenzene contaminated ground water, and organic carbon analysis results performed on ground water samples. This result is of interest since it was suspected that benzene and chlorobenzene were not detected in the soil gas samples due to aerobic biological degradation of these two compounds in the soil (8). One concern with the LGAS system has to do with the method of inserting the probe into the soil. By hammering the probe into the soil, compaction of soil around the sampling holes could potentially hinder diffusion of soil gas into the sampling probe. The primary advantages of this method are the speed with which soil contamination data is obtained due to on-site analysis, and the correlation of the results with ground water contamination for chemicals which are readily transported and stable in the soil gas.

The Lockheed passive sampling system (LPSS) has also been field tested for the measurement of chloroform, benzene, and chlorobenzene in soil gas (8). With the LPSS system, diffusional charcoal samplers were buried in a manifold about one foot deep for a sampling time appropriate for the expected soil gas concentration. The charcoal samplers were then removed from the soil, sealed in a container, and

transported off-site for analysis by gas chromatography. Data obtained using LPSS correlated with ground water chloroform levels and strongly correlated with the LGAS data, but failed to detect benzene and chlorobenzene in soil gas samples obtained above contaminated ground water. The LPSS samplers were left in place for a minimum of 14 days for this field study. This would likely be an unacceptably long sampling time for screening of waste sites for soil and ground water contamination. If the long sampling times necessary are acceptable, this method appears capable of yielding useful data.

The PETREX Surface Static Trapping Pyrolysis/Mass Spectrometry (SST-Py/MS) technique was the third technique field tested for the measurement of chloroform, benzene, and chlorobenzene in soil gas (6). This method uses a wire with a charcoal-coated tip, which is placed in a glass screwcap tube. The tube is opened and placed open end down in a one foot deep hole. The hole is filled with soil, and the sampler is left for a predetermined sampling time. The sampler is then retrieved, sealed, and transported to an off-site laboratory for analysis by pyrolysis/mass spectrometry. The results are reported in ion counts. The data obtained using the Petrex SST-Py/MS technique for soil gas measurement did not correlate with any of the target compounds compared to the relevant ground water concentration data. The observation of periodic patterns of peaks separated by 14 atomic mass units in the mass spectra obtained by this method indicate the presence of hydrocarbons in the soil gas could have interfered with the performance of the PETREX system. The PETREX samplers were left in place for 10 days for this field study. Again, this is usually an unacceptably long sampling time for screening of waste sites for soil and ground water contamination.

The soil-gas analysis technique which has been approved for use in the Department of Energy's (DOE) Environmental Site Survey (9) utilizes active sampling and sample collection with volatile organic sampling train (VOST) tubes coupled with analysis according to SW-846 Method 5040 (10). With this method, a sample probe is driven into the ground to create a one-inch diameter sampling hole. The sample probe is then removed. The hole is then left to equilibrate with the soil gases for a period of time, after which a VOST tube is placed in the hole and air is pumped through the tube. The tubes are then sealed and transported off-site to a laboratory for analysis. The analysis consists of thermally desorbing a VOST tube through five mL of organic free water onto the sorbent trap of a purge and trap sampling device. The purge and trap sorbent trap is then desorbed into a gas chromatograph and the sample detection is performed by low resolution mass spectrometry. This sampling and analysis technique relies on proven methodology, although analysis using Method 5040 is not necessarily a trivial matter. If too large a volume of sample is collected via this method, the gas chromatographic system can be overloaded and require downtime for cleanup.

There is another type of active sampling method which is being used to collect samples from DOE's Pantex facility that are being analyzed at

Oak Ridge National Laboratory (ORNL) as part of the Department of Energy Site Survey. A two inch diameter hole is drilled five feet deep. The hole opening is sealed and the soil gases are allowed to equilibrate for twenty-four hours. A solid sorbent sampling tube containing three different solid sorbent materials (11) is then placed in the hole with an air sampling pump. The hole is resealed, and two liters of soil gas is drawn through the sorbent trap. The sorbent trap is then sealed and transported to ORNL for analysis by thermal desorption/cryofocusing and gas chromatography/flame ionization detection. Concentration of the sample obtained by sampling two liters of soil gas should improve the sensitivity of these measurements versus the LGAS technique. Another advantage over the LGAS method is the fact that compaction of soil around the sample probe has been avoided, thus preventing the sampling process from being retarded. The use of three solid sorbent materials in the sorbent traps generates greater collection efficiency in general versus Tenax for the target volatile compounds, while avoiding the collection of less volatile organic compounds which would interfere with the subsequent sample analysis. One disadvantage is the necessity of transporting samples off-site for analysis.

Recommendations

Although no commercial systems designed for soil gas sample acquisition and analysis are presently available, there is now a commercially available soil probe for providing controlled access to depths of interest up to 20 feet, or 50 feet in unconsolidated soil. Geoprobe Systems of Salina, Kansas manufactures the Geoprobe Model 8A, which has a variety of penetration heads, along with an integral hydraulic hammer. The device is mounted in the back of a van, and is powered directly from the vehicle's crank shaft. Total price for the system, which includes a four-wheel drive van, is approximately $45,000. As more and more systems become available, this type of screening technique will exhibit increasing promise for the remedial investigation of waste sites for volatile organic compounds. An active sampling system with sample collection on solid sorbent traps will probably provide the most sensitive and reliable results. However, the fastest acquisition of sample results would occur with gas-tight syringe sample collection and on-site analysis. Triple sorbent traps have an advantage over VOST traps because the three sorbent materials would more efficiently trap a wider range of compounds than the Tenax and Tenax/charcoal VOST traps. In addition, the three sorbent traps are, in general, less susceptible to interferences than the Tenax and Tenax/charcoal VOST traps. The actual sensitivity obtained by this method would be affected by both the sampling methodology used and the characteristics of the waste site. Therefore, it would be essential to demonstrate the correlation of results from this method with groundwater or subsurface contamination at the target site as routine quality assurance precautions.

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SURVEY INSTRUMENTATION

Background

The principles for the instrumentation described in the following sections are based upon detection (for group screening measurements) or separation followed by detection (for the determination of specific compounds). The detection principles are the same whether for group screening or individual component determination. In photoionization detection, the organic compounds in the air sample or the gas chromatographic column carrier gas effluent are ionized by irradiation in ultraviolet light, and the migration of the resulting ions to the collector electrode is measured as an ion current. With the flame ionization detector, ionization is achieved by combustion in a hydrogen flame, and a similar ion current is measured. The response is proportional to the concentration of the compounds and to their ease of ionization. The catalytic oxidation detector relies upon the change in resistance of a platinum catalyst-coated resistive element when it is heated by the combustion of organic compounds on its catalytic surface. The electron capture detector operates on the ability of compounds to capture electrons from a carrier gas (argon/methane) ionized by a radiation source, and thus to reduce the standing current between two electrodes. Thus, in some respects, the final detection is the opposite of the ionization detectors, in that the existing signal decreases in the presence of the analyte. In contrast, most ionization detectors function by detecting an increase in the existing current when the analyte passes. Finally, the flame photometric detector measures the intensity of an optical emission from electronically excited decomposition products of (in this case) phosphorus-containing compounds as they are combusted in a hydrogen-rich flame.

The determination of specific compounds in complex environmental samples requires that the target compound be separated from other detectable compounds present in the sample. The technology selected in this assessment favors gas chromatography over liquid chromatography because of the ready availability of portable instrumentation, the higher resolution afforded by gas chromatography (particularly with capillary columns), and the highly sensitive and selective detectors available only in gas chromatography. In addition, liquid chromatography poses a problem of waste solvent disposal. However, where compounds exist which cannot be analyzed by gas chromatography, an alternative would be Thin-Layer Chromatography (TLC). In gas chromatography, the compounds in an injected sample are resolved by differences in their gas-liquid partitioning between the carrier gas and the stationary phase. The stationary phase, carrier gas and flow rate, and the column dimensions and temperature conditions are selected to maximize both the efficiency and selectivity of the separation, such that the particular target compounds being determined are resolved from potential interferences. With TLC, compounds migrate along an evaporating solvent front, according to their relative affinity for the solvent and the adsorptive medium on the plate. Detection systems for TLC, often colorimetric stains and UV induced fluorescence, are not as

sophisticated for quantitative determinations as are GC detector systems. Thus, it appears that TLC's use would be limited to that of a semi-quantitative tool.

In some cases (notably the pesticides), sample purification is a necessary part of the sample preparation procedure. This additional step is required to remove sample components which cannot be separated from the target compounds by the final analytical method, or which would eventually cause deterioration of the analytical system either by damaging the chromatographic column or contaminating the detector. Solid phase extraction columns are used to achieve these purifications by a combination of partitioning and adsorption.

Approach and Evaluation

This section presents the simplest field monitoring option: hand-portable monitors which provide a "total" group measurement of organic compounds.

Volatile Organic Compounds: Simple screening methods which measure total "volatile organic compounds" are already in use at many remedial action sites. These hand-held monitors determine total volatile organic compounds in air samples taken at the surface of freshly cored soil samples. The headspace over water samples also can be analyzed. In both cases, the volatile organic compounds in the sample are distributed between air and soil or water, depending upon their vapor pressures, and it is the vapor phase compounds which are measured as a group. The facile, on-site determination of total volatiles appears to be a most valuable means of rapidly screening samples to identify those containing appreciable amounts of volatile pollutants and thus requiring more detailed analyses. In some cases, correlations between results from soil core samples surveyed with hand held meters and volatile measurements made on the same samples have been poor (1), suggesting that such an approach has little utility for field investigations. However, studies in this laboratory of the preanalytical holding times of volatile organic compounds in soil (2) suggest that current sample handling and preservation techniques for off-site analysis are inadequate, and that the survey meters may be yielding a more accurate representation of the actual amount of volatiles in the soil than do the analyses performed a few days or weeks later. Thus, it may be that the only way to achieve accurate analysis of soil volatiles is to perform the determination in the field.

The total volatile organic compound survey monitors represent the most portable, rugged, and simple of the field monitoring options. The instruments are easy to use in the field because of their simple calibration (from a cylinder of compressed calibration gas) and readout (a meter; most also feature an adjustable audible alarm), light weight, and compact size. A good evaluation of the field reliability and performance for detecting fugitive emissions and of the ergonometrics of four of these instruments has been published as an EPA Report (3).

Nine portable total organic compound vapor survey meters are compared in Table 3. They utilize photoionization (PID), flame ionization (FID), or catalytic oxidation as the detection mechanism. The PID-based instruments additionally offer a choice of lamp ionizing voltages which can be used to control somewhat the selectivity of the monitor. The 10.6 or 10.2 and the 11.7 eV lamps are the most widely used because of their sensitivity. The sensitivity or detection limit specifications vary among the instruments, with the most sensitive being the 0.05 ppm (vol./vol.) for benzene achieved with the Photovac TIP I. The OVA-88 contains Tygon tubing which can adsorb sample components. It also may not be as sensitive as the other instruments. Note that the compound used to specify sensitivity is benzene, methane, or hexane. Intercomparisons of absolute sensitivity are difficult. Some data generated in the field (1) shows differences between the FID and PID-based instrument response to volatiles in soil samples. The reason for this is probably their different responses to aromatic and halogenated compounds (the PID exhibits a wider range of responses) and the detrimental effect of humidity on the PID response (4). For these reasons, the FID-based instruments are expected to produce more consistent measurements in the field where the relative humidity cannot be controlled. However, undetected flame-out of the FID could lead to false negative measurements. Precision appears to be quite good. "Calibration reproducibility" is reported (3) to be <1% for four of these instruments. All the ionization detectors achieve response times of a few seconds.

All the instruments are quite portable, weighing from 1.5 kg (3.3 lbs) to 6.8 kg (15 lbs). The heavier instruments, the Analytical Instrument Development, Inc. (AID) Model 590 and the Foxboro OVA 128, include a portable, ambient temperature gas chromatograph (GC). Although the GC allows more detailed characterization, the non-heated and un-thermostated column compartment is a serious disadvantage (see next section) which causes the target compound retention times to vary in the fluctuating temperatures of outdoor environments. An isothermal thermostating option allowing a very limited choice of temperatures is available for the Foxboro instrument, but it increases the weight which has to be carried around. All the instruments are completely self-contained. Their field packs, consisting of batteries (PID) or batteries and a compressed hydrogen cylinder (FID), permit operation in the field for at least 8 hours before recharging. In this regard, the PID-based instruments offer greater simplicity than the FID-based instruments. An additional approach is the measurement of total volatile organic halogen, an instrument available from Tracor. Although not strictly portable, the TVX monitor has low power requirements, and is lightweight. This instrument draws air through a sorbent tube, and desorbs the sample into a Hall Electrolytic Conductivity Detector (HECD). The halogens are converted to HX, and conductivity is measured. The instrument could therefore be used to monitor volatile halocarbons by purge, trap, and desorb, and semivolatile halocarbons by extraction, injection on an OV-101 trap, and desorption. Sensitivity should be in the 5-50 ppb range for both VOC and pesticides, although this will be affected by the concentration

factor. However, selectivity will be compromised by the bulk nature of the measurement property. This instrument would be attractive for remedial actions involving a small number of halocarbons and for site investigations.

Semivolatile Organic Compounds: No total semivolatile organic compound monitor is commercially available, although the TVX monitor described above could be used for pesticides.

Recommendations

The FID-based instruments are preferable for screening applications, primarily because of their relative insensitivity to water vapor and the greater consistency of their responses to different chemical classes. The AID 580 or 710 and the Foxboro OVA 108 or OVA 88 appear suitable, with the 580 and OVA 108 being preferred to the lower-model versions because of their greater sensitivity.

Studies are needed to relate the responses of these screening instruments to more detailed analyses conducted in the field (see next sections). Unresolved questions regarding the efficacy of current volatile organic sample handling and preservation methods suggest that the current data are not suitable for this comparison.

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CHROMATOGRAPHIC METHODS

Approach and Evaluation - Portable Instrumentation

This section focuses upon portable instrumentation which can be carried into the field and operated from a "lab camp" rather than being continuously carried around during the working day, as for the group monitors evaluated above. This option is intended to provide much more detailed analyses (i.e., of individual high priority organic compounds), and, hopefully, with the accuracy, precision, or sensitivity which might be achieved using laboratory-based instrumentation and procedures. Commercially available portable GC's are compared in Table 4.

Volatile Organic Compounds: The volatile organic compounds are separated by the GC column, which may be either a conventional packed column or one of the more recently introduced wide-bore (0.53 or 0.75 mm ID) capillary columns specifically designed for separation of volatile organic compounds. A good candidate for a packed column separation is 10 ft x 0.125 in (3 m x 3 mm OD) Teflon packed with 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport. With Ar carrier gas at 26 psi and a column temperature of 70°C, the primary target compounds benzene, trichloroethylene, and tetrachloroethylene would be separated from each other, as well as many of the secondary compounds, in approximately 11 minutes (1). The Supelco, Inc. VOCOL wide bore capillary column also is an attractive alternate which may offer more column efficiency, but perhaps less selectivity in the resolution between benzene and 1,2-dichloroethane. Also, the VOCOL column is glass, which may not be sufficiently rugged for field use. The separated compounds are detected and measured using a photoionization detector (PID) or a PID and ECD in series. The ionization potentials of these compounds (Table 2) indicate that the 10.2 eV lamp would produce optimum sensitivity. The 9.5 eV lamp would be more selective, because compounds with ionization potentials up to only ca. 9.8 eV would be detected versus the ca. 10.5 eV for the 10.2 eV lamp. However, this lamp also is 10-fold less sensitive for benzene than is the 10.2 eV lamp (2). (See instrument evaluation below).

The target compounds are determined by injecting 1 to 3 μl of the liquid extracts into appropriately equipped GCs. For dicyclopentadiene, the same (or an identical) GC as that used for the volatile compound analyses would be suitable. The column temperature would have to be raised by ca. 50°C to provide elution in a reasonable time period. The 7.74 eV ionization potential for dicyclopentadiene suggests that the PID with the 10.2 eV lamp would have good sensitivity. Conservative detection limits of ca. 10 μg/L in water and ca. 0.1 to 1 μg/g in soil might be achieved. Precision cannot be calculated, but may be 25 - 50%, depending on the characteristics of the samples and the severity of the environmental conditions.

Table 4. Comparison of portable gas chromatographs

Manufacturer:	HNU Systems, Inc.		Sentex Sensing Technology, Inc.		Analytical
Instrument:	301 P	321	Scentor	Scent-o-graph	210
Detectors[a]	FID, PID	Same	EC/AI, PID	Same	PID, ECD, TCDFID, PID, TCD, ECD w/AC, ECD, FPD
Inlet/valves[b]	GSV		GSV	Same	BFV, GSV, CSVBFV, GSV, CSV, neated GSV
Heated inj. & det.[c]	y-w/AC	y-w/AC	y-2/col	y-w/col	YY
Oven heating[d]	I-w/AC	TP-w/AC	I to 140°C	I to 140°C	I to 200°CI to 200°C
Column type[f]	PC or CC	PC or CC	PC	PC, MB	PCPC
Data system[g]	Int. avail.		Pr cmp avail.	Toshiba 1100[+] pr. cmp.	--
Dimensions, hxwxd, cm	26.7 x 34.9 x 27.9	Same	14.0 x 45.7 x 95.7	10.2 x 48.3 x 50.8	30.5 x 38.1 x 27.9 38.1 x 45.7 x 27.9
Mass, lbs/kg	25/11.3	Same	40/18.2	45/20.5	32/14.540/18.2
Field pack[h]	B, 2 g	-	B, Ar	B, Ar	B, GB, G

[a]FID = flame ionization detector. PID = photoionization detector. EC/AI = electron capture/argon ionization. TCD = thermal conductivity detector. FPD = flame photometric detector.
[b]GSV = gas sampling valve. BFV = backflush valve. CSV = column switching valve.
[c]w/AC = yes, if line power is supplied.
[d]I = isothermal. TP = temperature programming.
[e]Option allows 180°C.
[f]PC = packed column. CC = capillary column. MB = megabore (capillary) column.
[g]Int = integrator. Pr cmp = personal computer.
[h]B = battery pack. G = compressed gas tanks.
[i]AC = line power required. g = (compressed) gas required.
[j]b = operating time on batteries. g = operating time for carrier gas.
[k]Bz = benzene. ClHC = chlorinated hydrocarbons.
[l]Warranty for some parts may be less, e.g., 3 months for PID lamp.

Table 4. Comparison of portable gas chromatographs (Cont'd)

Manufacturer:	HNU Systems, Inc.		Sentex Sensing Technology, Inc.		Analytical Instrument Development, Inc.
Instrument:	301 P	321	Scentor	Scent-o-graph	210 511
Req'd field support[i]	-	AC, g		-	-
Operating time, hrs[j]	8	-	8 - b 8 - g	8 - b 32 - g	8 - b
Ambient conditions	≤40°C 20-80% RH	Same		0-45°	Same
Sensitivity[a,k]	5 pg Bz (PID) 100 pg Bz (FID)	Same	0.1 ppb Bz (PID) 0.01 ppm Bz (AID) 0.01 ppab ClHC (ECD)	Same 0.01 ppb SF_6 (ECD)	2 ppb Bz (PID)Same
Special features	-	-	-	Most capable data system	-Largest selection of valves. Only instrument w/FPD
Price, $K	ca. 7 3.3 Fa sp. phys. Model 4270	ca. 8	ca. 14	ca. 17	6-78-9
Warranty, yrs[l]	1	1	1	1 1	1

[a]FID = flame ionization detector. PID = photoionization detector. EC/AI = electron capture/argon ionization. TCD = thermal conductivity detector. FPD = flame photometric detector.
[b]GSV = gas sampling valve. BFV = backflush valve. CSV = column switching valve.
[c]w/AC = yes, if line power is supplied.
[d]I = isothermal. TP = temperature programming.
[e]Option allows 180°C.
[f]PC = packed column. CC = capillary column. MB = megabore (capillary) column.
[g]Int = integrator. Pr cmp = personal computer.
[h]B = battery pack. G = compressed gas tanks.
[i]AC = line power required. g = (compressed) gas required.
[j]b = operating time on batteries. g = operating time for carrier gas.
[k]Bz = benzene. ClHC = chlorinated hydrocarbons.
[l]Warranty for some parts may be less, e.g., 3 months for PID lamp.

The dibromochloropropane and the three pesticides are determined using a GC equipped with the ECD and either a packed or wide bore capillary column. The conditions for the pesticide determinations are fairly clear. The EPA-specified column (3), a 6 ft x 0.25 in ID (1.8 m x 4 mm ID) glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcoport held at 200°C, using argon/methane (95/5, v/v) as a carrier gas with a flow of 60 mL/minute, or the J&W DB-210+ Megabore column, 30 m x 0.53 mm ID, held at 170°C with 10 mL/minute helium (or argon/methane) carrier gas are suggested. The EPA-specified (5) packed column with the OV-101 phase also may be suitable. The dibromochloropropane is much more volatile than the pesticides, and its analysis would have to be conducted in a separate run on the same GC, but at a lower column temperature. It also might be possible to determine the dibromochloropropane in the same analysis as the dicyclopentadiene, but the sensitivity of the 10.2 eV PID lamp will be much worse than that of the ECD. Sensitivities of the method using the ECD under field conditions are difficult to predict, but 0.2 μg/l of water and to 0.002 to 0.02 μg/g in soil may be feasible. The sensitivity could be diminished if the field procedures for sample preparation are not sufficient to prevent serious contamination of the GC column and the ECD tritium foil.

The diisopropylmethylphosphonate would be best determined using a GC equipped with a phosphorus-selective detector, such as the flame photometric detector (FPD) or thermionic detector, although the PID may be sufficient. The thermionic (nitrogen - phosphorus or NPD) detector is not yet available in a portable instrument, and thus the FPD in the phosphorus mode is the only choice if strict portability is to be maintained. The suggested columns are a 15 m x 0.53 mm DB-1 Megabore column or a 1.8 m x 2 mm ID glass column packed with 3% OV-101 (or SP-1000 if chromatographic peak tailing is excessive with the OV-101 phase) on 100/120 mesh Supelcoport and maintained at ca. 175°C with a helium carrier gas flow of 10 (Megabore) or 25 (packed column) mL/minute. The sensitivity is difficult to estimate, but might be similar to that expected for the dicyclopentadiene analyses.

Excluded from this compilation are instruments which do not provide a heated column compartment. This exclusion is necessary because the retention times of the target compounds in the GC analyses are affected by the temperature of the column, and the field temperatures (and hence instrument temperatures and retention times) vary from hour to hour as well as day to day. The instrument calibrations would not remain constant. It should be mentioned that the Foxboro OVA-128 includes a GC unit which can provide chromatographic analyses either from the sampling probe or by gas syringe injection. Temperature control is achieved only with an optional "portable isothermal pack" consisting of an insulated passive thermal mass (aluminum block or supercooled mixture). Of the instruments which include an actively heated column compartment with adjustable temperature control, only the Sentex and Analytical Instrument Development, Inc. (AID) GCs provide battery-powered heating in the field. The Scentor, Scentograph, and the AID 210 and 511 are truly portable and self-contained, and they require no

utilities for ca. 8 hours of field use. The HNU GCs are suitable for use from a van or other facility having an electrical generator to supply line power. The HNU Model 301P is battery-powered, but does not provide for column compartment heating without line power. In addition, the Shimadzu Mini/2 GC, while designed as a laboratory unit and thus not listed in Table 4, is very compact and consumes only 6 watts of power.

As this document was going to press, HNU Systems, Inc., announced that it was preparing to market a new portable GC, the Model 311. The system has both packed and capillary column capability, and is outfitted with a photoionization detector. It has a heated column oven capable of temperatures between ambient and 200° C. However, operation is isothermal. It has both built-in air sampling and direct injection capability, as well as internal supplies for carrier and calibration gases. However, it weighs approximately 50 lbs, and must be powered by either line power or a portable generator. As such, the device, according to the criteria of this assessment, would be considered mobile, rather than portable. Quoted price for the device is $14,500.

The portable GCs are not as hand-carriable as are the screening instruments evaluated in the previous section, because of their much larger sizes and greater weights (up to 18.2 kg/40 lbs). They are mainly suited for being carried into the field and set up at a few central locations during the day for analysis of samples collected in adjacent areas. The Foxboro OVA-128 (Table 3), which also contains a GC unit, is the lightest (5.9 kg/13 lbs) of all the truly portable GCs.

For the volatile organic compound analyses, any of the Sentex or AID instruments would be suitable. The Scentograph is the most capable instrument because the Sentex PID has a much better sensitivity specification than does the AID PID and the integral personal computer data system allows automated calculation of results in the field. It also can store and employ multiple analytical programs for different analyses. This is expected to be important for a high-volume, rapid-turnaround field operation. It also would allow the data to be readily converted into "pollutant maps" in the field to guide soil excavation. However, the hardware allowing these greater capabilities considerably increases the price of the unit and possibly renders it less rugged than the conventional AID instruments. The AID models feature the most versatile valving, including a column backflush valve, although this might also prove less rugged. This valve decreases the time required between analyses by backflushing the less volatile, latest-eluting compounds out of the column after the compounds of interest have eluted.

For the determination of dibromochloropropane and the pesticides, either the Scentograph or the AID 210 or 511 are appropriate. Again, the column backflush valve of the AID instruments is an advantage, while the data system of the Scentograph greatly facilitates calculation of results. For the analysis of diisopropylmethylphosphonate, the only choice for a highly selective

and sensitive determination is the AID 511 because it is the only portable GC featuring the FPD. However, DIMP could also be determined by PID, since it has relatively high target detection limits.

Some developmental work is needed to optimize the sample preparation procedures and instrument conditions to be used in the field. These areas are noted in the above discussions. In order to conduct routine field analysis of a broad range of organic compounds, as many as three or four GC's might be needed, since a variety of columns, temperature programs, and detector systems would be required. The Scentograph is a highly capable instrument, but also the most expensive. It is suggested that one Scentograph equipped with the PID and ECD be tested for the analysis of the volatile compounds and the dicyclopentadiene. Two AID instruments are suggested, a Model 210 with ECD for the halogenated compounds, and a Model 511 with FPD for the diisopropylmethylphosphonate. One scentograph might do all volatiles, including DIMP, if equipped with PID and ECD.

Approach and Evaluation - Small instruments on a 4-Wheel Drive Vehicle

For the purposes of remedial action at any site of significant size, if three or four portable GCs are to be used, it is unlikely that these can be easily carried by the field personnel. Therefore, it becomes necessary to consider the logistics of getting to and from the site with all of these instruments. If a four wheel drive vehicle were available to transport these instruments to the site, it could also be equipped with an inverter or small portable generator to provide a limited amount of AC power. If this were the case, the options available for both sample preparation and analysis are increased. For example, the Soxtec extractor could be used as sold, and would provide sample preparation capability closely matched with the current laboratory practices for semivolatile and pesticides. In addition, there are alternatives to the truly portable GCs. The Shimadzu Mini-2 GC possesses full laboratory capability in a small package, including temperature programming, full microprocessor control, and a high degree of ruggedness. The power consumption is less than 10 watts, due to efficient insulation of the heated zones. Finally, the instrument would cost less than half that of a comparably equipped portable unit.

The ACAMS and MINICAMS instruments were designed under contract to USATHAMA for the purpose of monitoring extremely low concentrations of chemical agents in air. The technology used is very similar to that used in the Scentor GC's. A preconcentrator tube is used to collect organics from air, and to desorb the analytes into a GC oven. The instruments use wide-bore fused silica capillary columns. Detection is by flame photometry. The primary advantage of these instruments is their extreme ruggedness, as they were designed to operate continuously in rather harsh environments. They are not strictly portable (require AC power), but are small and easy to relocate. The primary limitation is the availability of detectors.

For these instruments to be useful for field analysis several modifications would be required. Ideally, detectors such as the FID, PID, and ECD should be available, and easily exchanged. Portability can probably be secured by the use of these detectors since the FPD is the primary consumer of power. More flexible control over the operating parameters would also be desirable. This control has been engineered out of the instruments to prevent accidental alteration. Finally, sampling systems would be required for the transfer of analytes from soil and water to the instruments (this is also true of the Scentor). However, if these modifications can be made, without sacrificing the inherent ruggedness, these instruments would provide an attractive alternative to the Scentor.

Another portable gas chromatograph which has been recently introduced is the Microsensor Technology, Inc.'s Model 203. This unit is particulary interesting, in that it can perform an analysis of volatile organics in less than one minute. It accomplishes this using micro engineering. The GC column is a 4 m fused silica capillary, while the detector is a micro thermal conductivity unit built into an integrated circuit chip. With a sample size of 1 nanoliter, its lower limit of detection for benzene is about 1 ppm. The unit's upper temperature operating limit is 200°C, but analyses are currently limited to volatile organics because it does not have a heated sample inlet. The Model 203 is considered an "environmental unit", having two complete inlet, column (one polar, the other non-polar), and detector systems, which sells for $7900. Data acquisition is accomplished using a personal computer. Because of its requirement for line power and lack of heated sample inlet, the unit is not ready to be fielded in a portable mode. However, the power consumption is very low (approximately 8 watts), and the use of a lecture bottle for carrier gas and a rechargeable battery pack would add less than 15 pounds to the overall weight. A lap-top computer could be used for data acquisition. The rapidity of analysis is the major attractive feature of the system, and such could be exploited for field use by combining with a purge and trap system, or some other system for concentrating the sample.

Approach and Evaluation - Van-Portable Automated Instrumentation

This option focuses upon achieving a high volume of the same type of analyses as described in the previous sections, using automated sample preparation and analysis instrumentation whenever possible. Several appropriate units are compared in Table 5. Because of the much greater weight of this equipment and the need for external utilities (mainly line power and compressed gases), the field portability of this option is limited to a van or a temporary hut in the field if a generator and compressed gas cylinders are available.

Non-portable equipment does exist for the static headspace method described in the previous section. The Carlo Erba and Perkin-Elmer devices are suitable for this type of sample preparation. Both devices are designed to thermostat soil or water samples in small (5 to 22 mL)

Table 5. Comparison of peripheral equipment for sample preparation

Manufacturer:	Foxboro	Tekmar		Carlo Erba	Perkin-Elmer	
Instrument:	Century programmed thermal desorber	Auto. dynamic headspace concentrator		Auto. headspace sampler HS 250	Automatic headspace injector HS-100	Headspace sampler HS-6
Features		Model 4100	Model 4200			
Type	Thermal desorber	Heated headspace	Same	Heated headspace	Heated headspace	Same
Oven temp., °C	100-350°C	to 200°C	to 175°C	to 120°C	35-150°C	40-190°C
Sample container volume mL	ca. 15	ca. 15	Same	5 or 10	22 (15)[a]	6 (2)[a]
No. of samples	1	1	10	40	100	6
Desorbed sample collected	300 mL tank	Sorbent trap	Sorbent trap	Vial headspace for syringe	Vial headspace for for pressurized needle	Vial headspace for for pressurized needle
Dimensions, hxwxd, cm	16.5 x 28 x 31.8	17.8 x 24.6 x 36.6	48.3 x 49.5 x 59.7	ca. 66 x 41 x 64	60 x 50 x 40	20 x 31 x 49
Mass, lbs/kg	20/9	22/10	75/34	ca. 40/18.2	93/42	11/5
Req'd field support[b]	LP	LP	LP, CA	LP, CA	LP	LP
Special features	Multiple analyses from collection chamber		UP to 10 samples can be preheated	40 samples can be preheated. Heated syringe.	Separate heating compartment allows all samples to be equilibrated for same time period before analysis. Magnetic stirrer accessory.	Pressurized sample withdrawal
Price, $K	6	ca. 9	ca. 15	ca. 13	ca. 19	ca. 5-6[c]
Warranty, yr	1	1	1	1	1	1

[a]Maximum usable liquid capacity.
[b]LP = line power, CA = compressed air.
[c]Depends upon specific Perkin-Elmer GC used for interfacing.

septum-capped vials and to inject aliquots of the container headspace into a GC. The Carlo Erba HS-250 utilizes a heated gas syringe, while the Perkin-Elmer HS-100 (or the nearly identical HS-101) and HS-6 pierce the septum with a needle, pressurize the vial with the GC carrier gas and force an aliquot of the headspace into the GC. This is claimed to prevent fractionation of the gas sample by avoiding the partial vacuum of a syringe. The Perkin-Elmer HS-100 is the most sophisticated of the devices. It features a microprocessor which allows multiple preparation methods. These include a constant equilibration time mode, in which the microprocessor transfers sample bottles from the magazine and into the thermostated compartment at the correct time such that each sample is equilibrated for the same time period before analysis. This feature would greatly improve the reproducibility of the analyses. The greater sophistication is achieved at the expense of ruggedness. None of these devices were designed to be portable, although the Carlo Erba HS-250 or the Perkin-Elmer HS-6 probably would tolerate field use better than would the HS-100. There is also an automated dynamic headspace device made by DANI, allowing heated dynamic stripping. This device is not sufficiently rugged for mobile use.

Semivolatile Organic Compounds: The manipulations required for preparation of water and particularly soil samples for analysis of the semivolatile organic compounds are not suited for automation at this time. The Varian AASP, which was designed for preparation of liquid samples for high performance liquid chromatographic analysis, is the only commercially available device for automated sample preparation which approaches the needs of this project with the exception of the previously mentioned Soxtec. The main opportunity for automation for the semivolatile organic compound analyses is in sample injection, data collection, and data calculation.

Automatic sample injectors for liquids have not been designed for the field-portable GCs, and laboratory GCs mounted in vans would be required.

Evaluation: The Carlo Erba HS-250 should be investigated for automating the volatile organic compound analyses in soil and water samples. It appears to offer reasonable simplicity and ruggedness as well as a high sample capacity (up to 40 samples). This device would have to be mounted in a van, and would require a laboratory GC (Carlo Erba Vega Series 2, ca. $13K) and a computing integrator (e.g., the Hewlett-Packard 3393A or the EM Science/Hitachi D-2000 for $2.5-3.5K) to complete the automated analysis package. Interfacing these automated devices with the field-portable GC is expected to be difficult and is not recommended. A lower-cost alternate to the Carlo Erba system is the Perkin-Elmer HS-6, a Perkin-Elmer Sigma 2000 GC (ca. $16K), and a computing integrator (as above). Some developmental work for optimizing instrumental conditions will be needed. Because these laboratory GCs can be temperature programmed, more rapid and efficient analyses can be achieved. Automation of the semivolatile

organic compound analyses is not possible without a major development effort.

Advanced Analytical Methods

This section concerns the development of advanced analytical methods which address some of the disadvantages encountered in the current analytical methods employing commercially available equipment. These disadvantages include:

(a) separate preparation methods are used in the analysis of volatile and semivolatile organic compounds,

(b) the efficiencies of the thermal and solvent extraction procedures are variable, and depend upon the properties of the samples as well as the target compounds,

(c) soil-bound residues of the target compounds (particularly pesticides) are not extracted and determined using conventional solvent extraction.

Improvements upon the current analytical methods would lead to increases in analytical sensitivity, accuracy, and precision, and decreases in analysis time and cost. Two areas for major technology application development are presented below.

Microwave Desorption of Compounds: This is a relatively new technology for recovering organic compounds from environmental matrices. The main advantage of the method is that the sample is heated very rapidly (periods of seconds) and thoroughly by the absorption of microwave power throughout its matrix, as opposed to the relatively slow rates of heating achieved conventionally by conduction and infrared radiation from an external heat source. It appears applicable to the problem of recovering volatile and semivolatile organic compounds from soil samples without the use of organic solvents or long heating times, or the need for a solid sorbent trap to concentrate the thermally desorbed compounds. A preliminary report (4) demonstrated the capillary column GC analysis of volatile organic compounds from a 150 mg sample of soil taken near a gasoline station. Water vapor in the sample is thought (4) to act as a "scrubber" which facilitates the desorption of "high boiling" compounds, suggesting that semivolatile organic compounds also might be recovered using this technology. The microwave desorption of semivolatile organic compounds from air particulate matter collected on filters is being studied (5).

Supercritical Fluid Extraction/Fractionation Integrated with GC Analysis: A fluid held at a temperature and pressure above its critical point is in the supercritical state. The specific advantage of supercritical fluids for this work is that they have the superior solvating power of condensed liquids and the lower viscosities and greater diffusion coefficients which approach those of gases. Reports of the extraction of organic compounds from soil (6), solid adsorbent

resin (7), and water (8) suggest that a supercritical fluid extraction could recover in a single procedure both volatile and semivolatile organic compounds for analysis. The density of a supercritical fluid has been programmed during an extraction to selectively mobilize different compounds (9). It may be possible to extract volatile organic compounds from soil and water with relatively low pressures of supercritical carbon dioxide or pentane before recovering the semivolatiles with higher pressures. Adding a concentration gradient of polar modifiers to the supercritical fluid may permit selective extraction of different classes of semivolatiles such as hydrocarbons and pesticides. The on-line interfacing (10) of supercritical fluid extraction and capillary GC demonstrates that these extraction procedures can be directly coupled with high resolution analytical methods to efficiently characterize complex samples. The combined supercritical fluid extraction/fractionation may eliminate the need for separate extraction and fractionation procedures for the volatile and semivolatile target compounds, and for the time-consuming concentration/purification steps.

Recommendations

Near Term: For group screening of soil and water samples for volatile organic compounds, the use of an FID-based instrument such as the Analytical Instrument Development, Inc. Model 710 or the Foxboro OVA-108 appears to be the most efficacious approach. Survey measurements of the total volatile organic compounds over soil and water samples should be compared with the results of on-site (field) analyses (see below) to establish the true relationship of such measurements to the actual content of the target volatile organic compounds and to determine the validity of such sample screening. The results of sample preparation using the Soxtec indicate that field use of that system would be appropriate.

For detailed analyses of the target organic compounds in the field three "portable" GCs would be needed. These are:

Volatile Organics and Dicyclopentadiene (possibly DIMP) - A Scentograph equipped with the 10.2 eV PID and ECD, the 180°C maximum oven temperature option, a wide-bore capillary column, and the heated inlet for syringe injection.

Pesticides and Dibromochloropropane - A Shimadzu Mini-2 GC with an ECD, column backflush valve, and a wide-bore capillary column. While this is not considered to be a field portable system, it appears to be sufficiently rugged and of sufficiently low power consumption so as to be fieldable. Power would be supplied from a small portable generator.

Diisopropylmethylphosphonate - An Analytical Instrument Development, Inc. Model 511 equipped with an FPD (phosphorus mode) and a wide-bore capillary column. The requirement for this system might be eliminated if laboratory evaluation

studies indicated that DIMP could be determined at its relatively high concern levels using a PID.

Developmental work to be conducted in the laboratory preliminary to the field studies include the optimization of the instrumental parameters for the separation and determination of the target compounds and the optimization of the sample heated headspace or solvent extraction and the solid phase concentration/purification procedures. Using local water and soil samples, the limits of detection, accuracy, precision, and sample throughput rate should be established. Evaluation of potential interferences would require on-site analyses or laboratory analyses of samples returned from the Rocky Mountain Arsenal site.

Long Term: The most readily-accessible of the technology development activities which would improve the efficiency of the field analyses is the automation of the heated headspace procedure for the determination of the volatile organic target compounds in soil and water. It is recommended that the Carlo Erba Model HS-250 automatic headspace sampler, a Vega Series 2 GC equipped with a 10.2 eV PID and a wide-bore capillary column, and a Hewlett Packard 3393A computing integrator be considered for eventual evaluation. The experience gained in the field studies (above) should allow this method to be set up and optimized quickly.

The microwave desorption and supercritical fluid extraction/fractionation integrated with GC analysis are longer-term but potentially offer a greater return in terms of increased analytical efficiency. It is recommended that the technology application development be initiated along with the near term work in order to bring this technology into line as soon as possible.

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SPECTROSCOPIC METHODS

Infrared Spectroscopy

A number of portable instruments based on infrared absorption are commercially available (e.g., Foxboro has at least five different models). These instruments typically use an internal sampling pump to pull air into the gas cell for analysis and to flush the cell when the measurement is complete. Filters are commonly used to monitor the specific wavelength required for the targeted compound. If single wavelength filters are employed, these filters must be manually changed to detect another compound. In some instruments, variable filters are used to scan the infrared region from 2.5 to 14.5 μm, eliminating the need to change filters manually. Some of these variable filter instruments are microprocessor controlled so that multiple compounds can be monitored. In addition, the microprocessor is used to store calibrations for a number of compounds (up to about 10) and a small library of infrared spectra of volatile organics.

These instruments are portable, weighing around thirty pounds, and powered by batteries. The sensitivity of the instrument depends primarily on the path length of the gas cell. Some gas cells have a fixed path length, while others have a variable path length which allows the sensitivity of the instrument to be changed. For a 20 meter gas cell, typical detection limits are 0.2 ppm for trichloroethylene, 0.08 ppm for tetrachloroethylene, and 2.2 ppm for benzene.

These infrared analyzers have several limitations for the field monitoring of organics. First, their detection limits are generally in the ppm and high ppb range, compared to low ppb range for mass spectrometry. Secondly, their specificity can be somewhat limited because often only one wavelength is monitored. This would allow other similar compounds to interfere. In addition, these instruments are limited to the detection of relatively volatile compounds, which would include benzene, trichloroethylene and tetrachloroethylene in the present study.

In addition to these portable infrared analyzers, combined gas chromatograph/infrared spectrometers are now available (including Digilab, Nicolet, Perkin-Elmer, Hewlett-Packard, Bomem and others) which can be run with a generator and could, for example, be mounted in a large van. The addition of a separation step prior to spectroscopic detection would greatly enhance the specificity of the measurement. However, the time of the analysis would also increase. An additional advantage of this approach is that these devices could be used to monitor all of the compounds on the targeted list, using the conventional sample preparation techniques already devised for the chromatographic analysis of these compounds. The detection limits of GC/IR at present is substantially higher than GC/MS.

Mass Spectrometry

Mass spectrometry is one of the most widely used analytical techniques for the analysis of organics in the environment, due to its high sensitivity and high specificity. A major limitation of most commercial mass spectrometers is that they are large and have large power requirements. A few commercial mass spectrometers have been devised specifically for on-site analysis (e.g., Bruker, Extrel and others). For example, one of these instruments (Bruker) is a small (8 ft^3, 300 lb) quadrupole mass spectrometer which is battery powered and requires no cooling water. It can be placed on a van for mobile monitoring. This instrument has a number of inlets which can be used to sample organics in air, in soil headspace, on surfaces, and in water. One probe uses a semipermeable membrane to detect ppb of organics in water directly. Another probe can be inserted in a hole to detect subsurface volatiles. A gas chromatograph may also be interfaced to the instrument to provide additional specificity. The GC used with this instrument uses a short column and the column is rapidly temperature programmed to complete the separation in the matter of a few minutes. The semipermeable membrane inlet is often used with the GC interface to analyze water samples directly with no sample preparation step. Bruker has recently introduced a more sophisticated GC inlet to the system. It has a more conventional length capillary column, and a built-in adsorption/thermal desorption cartridge for sampling and concentrating airborne contaminants. The detection limits of this device are comparable to conventional mass spectrometers used in EPA protocol.

A somewhat smaller device which operates on the same semi-permeable principle is the Aqua-Petra transportable mass spectrometer manufactured by VG Instruments, Inc. The organics in either the gas or liquid phase are introduced into the mass spectrometer by differential partitioning through the membrane. Gas samples are allowed to pass by the membrane, while water samples are pumped at continuous flow past the membrane. Otherwise, the mass spectrometric analysis is based on standard electron ionization technology and with a quadrupole mass filter and an electron multiplier. Data handling is accomplished with a portable computer. The unit weighs a total of 70 Kg and has a power consumption of 1 kW. Power can be supplied from batteries, from an available generator set, or from AC line power. Given the weight and dimensions, the unit would probably be operable from the back of a four-wheel drive vehicle. Thus, it would be useful as an adjunct to the portable gas chromatographs.

Given the relatively standard mass spectral instrumentation, the resulting spectra would be expected to match reasonably closely the spectra generated using laboratory GC/MS systems. Sensitivities are dependent on the partition coefficient of the particular analyte across the membrane, but are reported to be, for example, 0.1 ppb for lindane, 4 ppb for benzene, 5 ppb for tetrachloroethane, and 4 ppb for trichloroethane. These sensitivities compare favorably with the detection limits generally achievable with GC/MS, as they should.

Response times can be as low as one second. Sample preparation would be eliminated for water samples but would still be problematic with soil samples. It must be recognized that no preliminary separation is performed, as in the case of GC/MS, and therefore the probability of false positives is increased. However, the membrane inlet is strikingly similar to the membrane separator used in earlier GC/MS systems. It should be possible to interface a portable GC with this instrument in order to have a portable GC/MS system. Analyses currently carried out in the laboratory could be duplicated in the field. The total cost of the system is approximately $80K, which is quite reasonable. The flexibility inherent in the system combined with the power of mass spectrometry make this one of the most cost effective approaches to field analysis of organics. While there might be substantially greater development time required for the implementation of this system, it is recommended that this approach be investigated thoroughly.

Another type of mobile mass spectrometer which is commercially available (Sciex) uses two stages of mass spectrometry, MS/MS, to give the high degree of specificity typically obtained with GC/MS, but much more rapidly. A targeted compound in a complex matrix can be identified in a matter of seconds using MS/MS. This particular instrument employs atmospheric pressure ionization methods which allow the direct analysis of air samples. In addition, it has been used to analyze soil samples by thermal desorption. In this mode, a helical wire probe is used as a sample concentrator after the organics in the soil have been thermal desorbed. The detection limits of this instrument for organics in air are in the ppb to ppm range. Limitations of this system include the fact that it is very expensive (around $500-700K), is difficult to use for quantitative measurements, and requires sophisticated operational expertise.

A new type of environmental monitoring mass spectrometer ion source has recently been developed at ORNL which allows the direct mass spectrometric analysis of trace organics in air, water and soils. This ionization source is based on glow discharge and operates at a pressure of a few torr. The design of this source is very simple, making it rugged and easy to operate, as well as maintain. Air is sampled at a flow rate of a few mL per minute. Detection limits for organics in air have been measured routinely in the low ppb range. It can be operated in either the positive or negative ion mode, the latter of which provides enhanced sensitivity for halogenated compounds.

Recently, tests have been conducted using the glow discharge ionization source for the analysis of volatile compounds in water and soils. In the case of water, air is bubbled through the sample directly into the ionization source. Using this method, low ppb of trichloroethylene in water can be routinely detected. Soil samples have been similarly analyzed by placing 5 grams of soil in 10 mL of water, shaking and allowing the sample to equilibrate for a few minutes. Air is bubbled through the solution and into the ionization source. Low ppb levels of benzene in soil were readily detected using this technique. We have

begun comparing this technique with standard EPA methods for water and soil. Initial tests have shown that the glow discharge technique yields results in good agreement with the EPA methods; however, additional work will be necessary to fully evaluate the analytical capabilities of this new technique. We are also investigating the use of this source for the analysis of organics in the headspace of water and soil samples.

The glow discharge source could be readily interfaced to a small mass spectrometer for use in field situations. In addition, the source could also be interfaced to a tandem mass spectrometer (MS/MS) to provide more confident identifications of the targeted compounds without the use of a preliminary chromatographic step, as is done in GC/MS. Triple quadrupole instruments, as mentioned above, have been transported in vans for analysis of field samples. These instruments are large and complicated, but are generally reliable for the analysis of targeted compounds in environmental samples. The glow discharge source could be easily adapted to this type of instrument. Alternatively, the source could be interfaced to a new type of MS/MS, called an Ion Trap Mass Spectrometer (ITMS), which was developed by Finnigan. This instrument is small and would be more mobile than a triple quadrupole instrument. In addition, it should be easier to operate and maintain and is less expensive than a conventional MS/MS instrument. The interfacing of the glow discharge source to an ITMS has not been attempted, but should not present a great problem.

Piezoelectric Detectors

Quartz piezoelectric crystals may be coated with a substrate to detect small amounts of adsorbed materials by inducing changes in the frequency of the crystal. These devices have been in existence for a number of years and substrates have been devised to selectively detect a variety of compounds, including organophosphorus compounds, such as diisopropylmethylphosphonate (1). These devices are small, portable and inexpensive and can typically detect low ppm of materials in air.

With improvement in the detection electronics, these detectors could be made even more sensitive. Additional substrates need to be devised for detecting a wider variety of compounds or classes of compounds. It is believed that a complete portable unit for field measurements weighing about three pounds could be constructed, which would include sampling mechanism, detector(s), and LED readouts. A small internal heater would be used to desorb material from the substrate prior to the next analysis. A card could be devised to hold the crystal sensor array, which would plug into the unit and could be readily changed to detect other compounds.

Other Spectroscopic Techniques

A number of other spectroscopic techniques have also been devised to detect organics in environmental samples, particularly in air. Derivative ultraviolet absorption spectra (DUVAS) has been used to

detect benzene and other organics in air and detection limits of 0.06 ppm for benzene has been achieved (2). Ultimately, the selectivity of this technique might limit its usefulness for monitoring specific compounds, however. Tunable atomic line molecular spectrometry (TALMS) has been used for benzene and other organics, but is still in developmental stages (3). Multiphoton ionization techniques with supersonic jets have been used to detect traces of benzene in gases (4). This technique is quite complicated and would not be amenable to field use. Low temperature luminescence techniques can also be used to detect organics, but these techniques are also not readily portable (5).

Recommendations

Identification and Quantitation:

As far as single analytical techniques are concerned, mass spectrometry would give the best combined identification capabilities and detection limits available from current analytical technology. Mass spectrometers can rival the detection limits of electron capture detectors for the analysis of halogenated materials when used in the negative ion mode. The major limitation of mass spectrometry for the analysis of the list of targeted compounds is that direct sampling of the compounds from the environment would be generally restricted to volatiles. Other compounds would need to be processed prior to analysis in a fashion similar to chromatographic methods. However, it is claimed that the membrane sampler on the Bruker and the VG Petra-MS instruments can analyze volatiles as well as semivolatiles in soil and water samples directly. These devices are relatively new and would need to be tested further before a recommendation for their use for both quantitative and qualitative analyses could be made.

Of the small commercial mass spectrometers currently available, few have been thoroughly field tested for any length of time. Before one of these instruments could be recommended for routine field use, these instruments would need to be tested for actual sensitivity, ease of operation and maintenance, and other characteristics. The Bruker instrument is moderately expensive (about $200 K), whereas the VG system is more reasonable ($80K). To obtain the best compound specificity, any instrument based on a single mass analyzer would need to be operated in tandem with a gas chromatograph (i.e., as a GC/MS), which would increase the analysis time considerably. The Bruker instrument, with the recently introduced true GC sampling head,. would be likely to achieve the greatest compound specificity.

By using a triple quadrupole MS/MS, such as the Sciex instrument, one could obtain significantly better compound specificity in a very short period of time. However, this instrument is generally thought of as a means of scoping an environment for the presence of a targeted compound, and not for determining quantities present. Its major limitations are its complexity and size, inability to use for more than an eight hour period due to the requirement of recycling the cryogenic

pumps on the ionization source, and the substantial cost of the instrument ($500,000-700,000, depending upon options).

The new concept of combining glow discharge ionization with a triple quadrupole instrument would eliminate most if not all of the limitations of the Sciex system. The performance of this device has been demonstrated on a single quadrupole instrument. Further development time (a year or less) would be required to fully evaluate its operation on a triple quadrupole instrument. This instrument could be produced for substantially less than $200K if the glow discharge source were coupled to a IT/MS, which has recently been developed and is commercially available. The simplicity of this glow discharge-IT/MS would allow it to be run essentially continuously.

Both the glow discharge source and the IT/MS are mechanically simple, allowing them to be maintained in the field quickly and with a minimum of facilities. It is possible that a membrane device could be used with this instrument to allow it to sample semivolatiles from air and soil samples, as well.

Chromatographic-based techniques are inexpensive, simple to use and yield good quantitative results, but only if the identity of the compound is known and only if the chromatographic peak is fully resolved. Use of a mass spectrometer eliminates these ambiguities, whether it is used as a GC/MS or as a MS/MS. Mass spectrometry-based techniques yield much greater compound specificity than conventional chromatographic detectors.

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IMMUNOASSAY TECHNIQUES

Background

Over the last thirty years, immunoassays have been developed and used for a variety of analyses. The general property of these assays is high sensitivity and rapid analysis. The usual drawbacks include a lack of specificity and available reagents. For these reasons, immunoassays have found their greatest utility in clinical analysis, where a very large number of samples of similar nature are analyzed, and where limited sample size is available (1-4). Since this is not the usual case in environmental analysis, these techniques have not been used to any great extent, although a variety of applications have begun to appear (5-9). Immunoassays fall into three general categories: radioimmunoassay (RIA), enzyme immunoassays (EMIT and ELISA), and immunoassays based on fluorescence detection (4,10). In all cases, detection and quantitation are performed using conventional methods. As such, none of these systems represents a truly portable analysis, and can very well require sophisticated measurement systems. Only recently have strides been made in the use of these techniques in environmental field settings.

Conceptually, immunoassays are based on antibody-antigen interactions, with an antibody tailored to a specific analyte (antigen) required. In recent years, the use of monoclonal antibodies has greatly increased the utility of these methods due to an increase in the ease of antibody production as well as the increased selectivity inherent in the monoclonal approach. The development of an immunoassay for a particular analyte requires the production of the antigen -- small molecules cannot be used as such and must be bound to larger molecules prior to development of the antibody. This requires considerable synthetic effort and cannot always be done without loss of selectivity. The next step is the production of the antibody. Finally, the assay conditions must be developed. Thus, a single component assay requires considerable up-front development time. The obvious advantage is the high throughput and high sensitivity which are the result of this development. The primary utility of immunoassays is in screening of large numbers of samples for a single component. Due to the limitations imposed by the measurement systems, enzyme immunoassay using colorimetric detection appears to offer the greatest hope for routine field operability.

Approach and Evaluation

Enzyme immunoassays for the determination of toxic components in environmental samples is, as alluded to earlier, still in its infancy. To date, there are only a few environmental components for which enzyme immunoassay methods are available (5-9). Whether these methods can be used in a field setting at the current time is problematic. Furthermore, almost all immunoassays require that the sample be presented to the system in an aqueous liquid. Thus, the primary use would be for water samples. Soil analysis using an immunoassay

technique would require some novel form of sample preparation, which might be more difficult to perform in the field than the available methods mentioned in the earlier section, and which would almost certainly require additional sample preparation time. However, the benefits of a properly engineered immunoassay system could far outweigh these drawbacks.

For the purposes of the target compounds considered in this technology assessment, no commercially available immunoassay methods exist. Westinghouse Bio-Analytic Systems has developed such methods for other compounds (pentachlorophenol), and could possibly develop custom immunoassays for the compounds of interest. The expected cost of such development is from $30,000 to $60,000, depending on the degree to which sample extraction methodology development is required and the level of extraction difficulty. Due to the fact that most of the components of interest are nonpolar, with low water solubility, and that many of the samples will be soils, it would appear that the cost for these compounds would approach the upper figure. The required instrumentation (plate reader, personal computer, printer and software package) would cost approximately $20,000. Sensitivity is expected to be in the low ppb range without sample concentration but is dependent on the affinity of the antibody to the analyte and will vary from compound to compound.

An additional factor for consideration is the turnaround time. While throughput can be very high, most enzyme immunoassays will require incubation time. This may be as much as several hours. Thus, while many samples can be processed simultaneously, the time required for production of the final result will be on the order of hours. Additionally, an immunoassay will be required for each analyte which must be determined. The logistical aspects of these systems could preclude their use except in cases where only a few analytes must be determined in a relatively large number of samples. Nevertheless, for analytes which do not behave well when analyzed by GC or GC/MS, the development of an immunoassay method may well be cost effective. As these methods become available, it would be prudent to evaluate their utility in the field.

Recommendations

No commercially available immunoassay systems exist for the determination of the target compounds of this assessment. In addition, the technology has a number of drawbacks (aqueous media only and considerable turnaround time) which would suggest that it would be quite some time before the methodology would be of utility for remedial action investigations. However, its potentially high specificity and high sample capacity suggest that it may be of some value for site investigation studies in the future.

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SUMMARY RECOMMENDATIONS FOR ORGANIC ANALYSES IN THE FIELD

Regardless of whether the field determinations of organic analytes are performed at RMA or elsewhere, the analytical methods required are similar. Volatile organics must be measured in water and soil, as well as possibly in air. Semivolatile organics, including pesticides, must be determined in both water and soil as well. However, there is a difference between the strategy for organics and inorganics in that many of the determinations currently performed in the laboratory can be performed in the field using commercially available instrumentation. Thus, it is possible to duplicate laboratory capability in the field at the present time. The advantages to be gained by this approach include rapid deployment, high probability of comparability of field and laboratory values, and the use of proven technology. The drawbacks are essentially those of the laboratory methods, with the exception of the sample transport limitations. Since it is likely that at any remedial action site several methods will be needed, it is recommended that a vehicle capable of housing the required instrumentation be equipped with an inverter or small portable generator and outfitted to perform the analyses. This is not to be construed as recommendation for the establishment of a motor home-sized mobile laboratory. Rather, we would recommend that space be made available in the back of a four-wheel drive vehicle or camper-topped pick-up truck for secure placement of the equipment.

For the volatile organics, the preferred technique is purge and trap sample preparation, followed by gas chromatography. The instrument recommended is the Scentograph or Scentor portable GC, since the sample preparation is built-in, and truly portable operation is still an option. Both soil and water samples can be analyzed in this manner, and the highest possible sensitivity can be obtained without precluding the use of less sensitive techniques such as headspace analysis or direct injection. It is entirely possible that this instrument could perform a large percentage of the analyses required in the field, regardless of the nature of the contamination.

For the semivolatile organics in water, the sample preparation technique recommended is solvent partition using the Mixxor device, with solid sorbent extraction also highly recommended where appropriate. The sample preparation technique for soils and other solid samples is the use of the Soxtec system. The analytical instrumentation chosen for the determination of the semivolatiles is highly dependent on the compounds present at a particular site. However, the more complex nature of the mixtures usually encountered, combined with the expanded temperature range, requires more sophisticated chromatographic systems than does the analysis of the volatiles. The more appropriate choice for these compounds appears to be an analytical GC with full laboratory capability, but still possessing the necessary ruggedness and limited size. The instrument of choice for this purpose is the Shimadzu Mini-2 GC. This instrument should allow the determination of any and all semivolatiles on the current Hazardous Substances List.

The approach described above allows the rapid deployment in the field of an analytical capability sufficient to meet the needs of the Rocky Mountain Arsenal investigation. However, the approach clearly does not meet all of the objectives of field analytical chemistry. It appears that the area capable of making the greatest impact in the near to medium time frame is mass spectrometry. However, more detailed laboratory validation of instruments such as the VG system is necessary prior to field testing. It is recommended that this validation take place concurrently with the deployment of more conventional analyses based on gas chromatography.

As more methodology for immunoassay determination of environmental contaminants becomes available, this will undoubtedly have an impact on the strategy outlined above. However, the fact that field measurements can be carried out immediately by more conventional techniques will enable an even more cost effective evaluation of new immunoassay methods. It is recommended that any immunoassay methodology capable of determining RMA target analytes be evaluated as soon as that method is available.

APPENDIX A

Physical Properties of Nine Target Organic Compounds Found at the Rocky Mountain Arsenal

Table A-1
Physical properties of nine target organic compounds found at the Rocky Mountain Arsenal Site

Compound	Mol. form.	Structure	Mol. wt.	CAS No.	M.P. (°C)	B.P. (°C)	Vapor press. (Torr)	Sol. in H_2O (mg/L)
Benzene	C_6H_6	0	78	71-43-2	5.5	80	76 (20°C)	1780 (20°C)
Trichloroethylene	C_2HCl_3	$ClCH = CCl_2$	131	79-01-6	-87	87	60 (20°C)	1100
Tetrachloroethylene	C_2Cl_4	$Cl_2 = CCl_2$	166	127-18-4	-22	121	14 (20°C)	150 (25°C)
Dicyclopentadiene	$C_{10}H_{12}$	CH_2	132	77-73-6	33	170-172	10 (40°C)	-
Di-isopropyl-methylphosphate (DIMP)	$C_7H_{17}O_3P$	o CH_3-P o-isoC_3H_7 o-isoC_3H_7	180	1445-75-6	-	89 (18 Torr)	2 (70°C)	-
1,2-Dibromo-3-chloropropane (DBCP)	$C_3H_5Br_2Cl$	$ClCH_2CHBrCH_2Br$	236	96-12-8	-	196	0.8 (21°C)	1000
Aldrin	$C_{12}H_8Cl_6$	Cl Cl CCl_2 CH_2 Cl Cl 1,4-endo-exo-5,8	365	309-00-2	104	-	7.5×10^{-5} (20°C)	0.01
Dieldrin	$C_{12}H_8Cl_6O$	Cl Cl CCl_2 CH_2 O Cl Cl 1,4-endo-exo-5,8	381	60-57-1	176-177	-	3.1×10^{-6} (20°C)	0.1
Endrin	$C_{12}H_8Cl_6O$	Cl Cl CCl_2 CH_2 O Cl Cl 1,4-endo-endo-5,8	381	72-20-8	245 (doc.)	-	2×10^{-7} (20°C)	-

APPENDIX B

Evaluation of Capital Equipment Recommended for Use as Fieldable Analytical Technology at Rocky Mountain Arsenal

Evaluation of Capital Equipment Recommended for Use as Fieldable Analytical Technology at Rocky Mountain Arsenal

As a result of the technology assessment described in the body of this report, a number of recommendations have been made as to equipment which should be acquired to perform field evaluation studies. Various features of selected fieldable or portable instrument types are compared in the attached tables. In general, instruments have been listed in the order of their utility to the project, without regard to cost. Specific recommendations are justified briefly below. Additional information can be found in the text of the assessment of various technologies. Evaluation of laboratory type equipment has been specifically omitted from the comparison, except where it has been recommended as a preferred alternative to commercially available portable instrumentation.

Features of the only commercially available microwave digestion system are presented in Table B-1. Essentially, the primary alternative to MDS-81D Microwave Digestion System is the use of manual digestion on a hot plate system. Such an approach has the following drawbacks: Use of larger quantities of corrosive acids, disposal of acid fumes, and much longer times required for sample preparation. The only important limitation of the microwave approach is the limited sample size and the need for ac power in the field. However, for soils, sample size is not expected to be a problem, since the analytical methods being recommended are sufficiently sensitive to compensate for this at the concern levels given in Table 1. Another possible alternative for digesting soil samples is the proprietary flux marketed by Scintrex, called Geoflux. Although some development effort would be required, along with the occasional use of an open flame, the use of this material may offer an attractive alternative to both microwave and conventional digestion in the field.

Three atomic absorption systems potentially suitable for use in the field are compared in Table B-2. The Scintrex unit is recommended for acquisition over the other units because of its compact design, its need for only one supporting gas cylinder and its flameless operation. The Perkin Elmer system, while it is extremely rugged, will determine only one of the four target metals, possesses limited sensitivity, and its built-in sample processor would be expected to have limited utility for soil samples. The Buck system, while less expensive, and possessing comparable sensitivity to the Scintrex unit, requires two cylinders of supporting gas (one of which is flammable), and appears to be insufficiently rugged for field use. Heat and exhaust gas dispersion in an enclosed vehicle might also be a limitation of the latter system.

Three systems for the quantitative determination of mercury vapor are compared in Table B-3. All of the surveyed instrumentation require the independent generation of cold mercury vapor prior to its instrumental determination. Depending of the chemical state of mercury in the water or soil, this could be as straightforward as heating the sample to

drive off elemental mercury, or as complex as digestion under non-reducing conditions. The Jerome Instruments gold film amalgamation meter is recommended over the more conventional dedicated AA instruments because of its true portability (other instruments require external power) and its factor of 10 greater sensitivity.

Several systems for the determination of arsenic as arsine vapor are commercially available. Four portable or field useful instruments are compared in Table B-4. The Riken Model AS-7 is recommended for acquisition over the other units based on its being battery operated, having a span of 0-1 ppm with digital readout and its lower cost. The Sensidyne unit ($3400) would be a good second choice and its alternate range of 0-5 ppm might be useful but the additional cost may not be justified. Both the Riken and the Sensidyne use controlled potential electrolysis cells which are generally considered more rugged than gas membrane galvanic cells as used in the CEA TGA4000P. The tenfold greater sensitivity of the TGA4000P, while an asset in many applications would actually be a liability here since ppm levels are anticipated. The very limited span of the MDA TLD-1 unit of 25-150 ppb would prove a handicap, even with input dilution, since it does not read down to zero. While the stated accuracy of the TGH4000P and the Riken AS-7 is ±5% compared to ±8% for the Sensidyne SS4000 this is not considered to be significant. The practical accuracy is dependent on periodic field calibration. The MDA unit has no provision for field calibration (no span and zero adjust), and is fixed by Chem-Cassette composition.

Portable or fieldable x-ray fluorescence units are compared in Table B-5. The recommendation for choice of an XRF system is complicated by the competing strengths and limitations of each system. First, if portability is critical to the application, then the choice is really limited to three of the instruments surveyed, the CSI X-Met 840, the ASOMA Instruments 8620, and the Oxford Analytical Lab-X 1000 series. The CSI unit is somewhat older technology, but consequently, has more documentation as to its performance in the field. It is the most expensive of the three, but has a separate sampling head which can bring the probe into direct contact with soil. However, since the overall sensitivity of the unit is less than the concern levels for the target species, it is unlikely that the hand held probe would be frequently used. Instead, soil samples would be removed from the ground, dried, homogenized, and measured, in order to maximize sensitivity. The ASOMA unit is half the cost of the CSI system, but it has no hand held sampling probe. This forces the requirement of more sample handling, even with more heavily contaminated samples. Also, the ASOMA unit can be used in a screening mode, in which the sum of HG, AS, and PB can be determined down to 25 ppm. This level is a factor of two to three below the LOD for the CSI instrument. This may be a particularly attractive feature for remedial action sites, in which it may not be as important to know the nature of the contamination as it is the extent of the contamination of any of the target species. Both the CSI and the ASOMA units function essentially as "black boxes." That is, the sample is placed in the measurement cup, and the

instrument prints a result. There is no opportunity for the operator to view the instrumental response. The latter is a unique feature of the Oxford Analytical line of XRF systems. The 1000 Series instruments are reasonable light weight systems (ca. 41 lb) which have a 256 channel analyzer and which allow the x-ray spectrum acquired to be displayed on a liquid crystal display. This is an important advantage, in that it permits the operator to view the presence of potentially interfering elements, and take appropriate action. The unit has a sensitivity which is comparable to the CSI unit, except for HG. In this case, the CSI system is claimed to have an LOD in the high 100's of ppm range. Oxford Analytical claims an LOD for HG between 100 and 200 ppm. Also, the Oxford system is not as portable as the CSI system. It is considerably heavier, and is designed to operate on line voltage. However, its power consumption is sufficiently low than it would seem relatively straightforward to fabricate a small invertor and a battery pack which could power the instrument for five hours between rechargings which would be sufficiently small to be carried into the field. Also, the Oxford unit is about one-third the cost of the CSI unit. Thus, the recommendation as to which of the portable systems depends heavily on the specific intended use of the XRF system, cost, and the nature and extent of possible interferences. Any of these systems would be recommended over the other units described. First, they possess superior sensitivity, are capable of being easily moved and powered without a generator. In addition, no external coolant is required, and the sample compartments, because of their configuration, would be more compatible with filter paper in those applications where concentration of the trace metals was performed through co-precipitation and filtration.

For the determination of organic species in the field, basically two analyses to be performed: volatile organics and semivolatile organics. Thus, two gas chromatographs will be required. Portable or field useful GC's are compared in Table B-6. For the volatile organics, the choice is relatively clear. The Sentex units are unique in their capability to perform the preconcentration necessary to meet the goals of the program. If any other unit is purchased, it will require development of external purging equipment. While this development is not extremely difficult, no commercially available portable device exists. The use of the Sentex unit will allow truly portable operation, with the only additional equipment being a purging device (available from many sources). The unit will not be limited to the analytes specific to RMA, but will be useful for all volatile organic compounds.

For the analysis of semivolatile organic compounds, the choices are obscured by the fact that sample preparation will be required. For water samples, a simple solvent extraction should be sufficient to meet sensitivity goals. This might not be the case if detection limits were significantly lowered, or if the goal was to analyze large numbers of samples simultaneously. In either of these cases solid phase extraction would be preferred. For the semivolatile organic compounds in soil, the Soxtec extractor appears to offer the best hope of

providing timely extraction without large solvent requirements. As many as twelve units could be used simultaneously. This is the only currently commercially available instrument useful for soil extraction. The alternative to the Soxtec is a soxhlet extraction, the time and solvent supply for which make its use in the field impractical. Since the Soxtec extractor will operate best using AC power, and since equipment required for inorganic analysis will require some AC power, the gas chromatograph selected for semivolatile organic analysis is the Shimadzu Mini-2. This unit is as small as the truly portable units (see attached table), has very low power consumption, and possesses full laboratory capability. This is important since the portable units have limited upper temperature ranges. While it is entirely possible to use column technology to reduce the requirements for elution temperature, the Shimadzu has the ability to more closely duplicate the current laboratory methods. In addition, it is considerably less expensive than the portable units.

"Portable" or fieldable mass spectrometers are compared in Table B-7, although they are not recommended for acquisition at this time. The system of choice currently is the VG. There are several reasons for this choice, including relatively low cost, small size, and ability to interface directly with a gas chromatograph. The instrument has proven ability to detect pesticides in water. However, considerable effort will be required to meet the program goals using this instrument, particularly in the analysis of semivolatile organics in soil. The analyzer is specifically designed for water analysis, and considerable development effort would be required to conceive, design, build, and evaluate a sampling technique for soils. However, such an approach offers the organic equivalent of an XRF system, in that actual hands on sample processing would be minimized with such an approach.

Table B-1

Description of Microwave Digestion System

Instrument	Approx. Cost	Size (in^3)	Weight (lb)	Support Required	Strengths	Liabilities
CEM MDS-81D	$8500	6210	80	115 vac, 1800 watts max	Much higher speed digestion of environmental samples	Limited sample size (500 mg soil, 50 ml water) Requires external power

Table B-2

Comparison of "Portable" Atomic Absorption Spectrometers

Instrument	Approximate Cost	Size (in^3)	Weight (lb)	Support Required	Strengths	Liabilities
Scintrex Model AAZ-2	$20,000	970	57	Pressurized argon 115 vac/500 watts	Compact, ruggedized All target elements except Hg, several other elements Zeeman corrected background eliminates need for deuterium lamp Flameless operation Detection limits comparable to laboratory systems	Lamp changing required
Buck Scientific Model 200A	$ 8,000	1925	36	Pressurized acetylene or pressurized air or N_2O 115v/AC 30 watts	Inexpensive Detection limits comparable to laboratory systems All target element except Hg, several other elements	Requires high precision optical alignment (high resolution optics) Not particularly rugged (eg. exposed lamp socket) Exposed flame may cause heat buildup problem Lamp changing required
Perkin Elmer Portable Wear Metal Analyzer	$60,000	7128	76	115 vac	Extremely rugged, built in argon cylinder Built in sample processor for oil samples	Limited sensitivity Applicability to acid digested samples unknown Applicable for only one(Copper) of the target metals

Table B-3

Comparison of "Portable" Mercury Vapor Analyzer

Instrument	Principle of Operation	Approx. Cost	Size (in^3)	Weight (lb)	Support Required	Strengths	Liabilities
Jerome Instruments Model 411	Gold Film Amalgamation	$4000	312	5	None-Rechargeable Batteries	High Specificity High Sensitivity (1 ng limit of detection) True Portability	
Buck Scientific Inst. Model 400	Atomic Absorption	$3000	1540	18	115vac, 80 watts	Technology identical to that already accepted High Specificity Absolute detection Limit:10 ng	External power required
Spectro Products Model HG-4	Atomic Absorption	$4000	1600	25	115vac, 100 watts	Technology identical to that already accepted High specificity Absolute detection Limit:10 ng	External power required

Table B-4

Comparison of Portable Arsine Detection Instruments

Instrument	Approximate Cost	Size (in^3)	Weight (lb)	Support Required	Strengths	Liabilities
Riken Model AS-7	$1995	159	5	None	Unit is self contained with pump, battery pack and digital readout. Range is 0-1 ppm. Instantaneous readout as well as signal averaging is provided.	Unit does not incorporate flow indicator
Sensidyne Model SS4000	$3400	131	5	None	Spans of 0-1 ppm and 0-5ppm are available and changeable in field. Unit is self contained with air pump, readout meter battery pack. Stated overall accuracy of instrument is ±8%.	Unit does not incorporate flow indicator
CEA Model TGA 4000P	$4495	832	13	115 vac	Self contained with internal air sampling pump, flow indicator and signal readout meter. Stated overall accuracy ±5%.	Fixed span of 0-100 ppb would require calibrated input dilution for use on higher AsH_3 concentrations. Servicing or replacement of sensing cell required at six month intervals.
MDA Model TLD-1	$3495	381	9	None	Unit uses chemical cassette optical detection system, manufacturer claims field calibration is not necessary. Integral recorder available.	Limited fixed span of 25-150 ppb. Higher level would require calibrated input dilution. Periodic chem-cassette tape change necessary. Unit does not incorporate flow indicator Stated overall accuracy of instrument is ±20%.

Table B-5

Comparison of "Portable" X-Ray Fluorescence Analysis Systems

Instrument	Approximate Cost	Size (in^3)	Weight (lb)	Support Required	Strengths	Liabilities
Columbia Scientific X-Met Model 840	$50,000	Probe: 85 Control Unit:1100	18	None (Rechargeable Battery Pack)	All target elements analyzeable with one source True portability Configuration of sample compartment compatible with filter paper	Limit of detection about 90 μg/g
Oxford Analytical Model L1005	$15,000	Unknown	41	115 VAC or Battery Pack/ invertor	Inexpensive Multichannel analyzer w/ direct readout	Development of Power source required No sample probe head
ASOMA Instruments Model 8620	$25,000	1400	18	115 VAC or Battery Pack	Inexpensive Greater sensitivity for Pb, As, & Hg combined	Lower sensitivity for individual As, Pb, & Hg No direct probe head
Cianflone Scientific Model 2501 Portaspec	$18,500	Power supply: 2000 Probe:500	73	Cooling water Forced air power supply cooling 115 vac, 300 watts	Inexpensive	Considerable support requirements Detection limits only to 500 μg/g for most elements Rather short (9 ft.) cable precludes remote sampling
Kevex Model 6700 Controller with X-SITE 9900 Portable Probe	$40,000	Controller:4650 Probe:600	58	Liquid nitrogen 115 vac,400 watts	High resolution detector 75' cable permits controller unit to be remote from sample probe	Limits of detection about 1000 μg/g Requires liquid nitrogen for probe coolant

Table B-6

Comparison of Fieldable Gas Chromatographs

Instrument	Approximate Cost	Size (in^3)	Weight (lb)	Support Required	Strengths	Liabilities
Sentex Scentor	$14,000	3736	40	None	Portable, Preconcentrator for Volatiles	Limited temp. range
Sentex Scentograph	$17,000	1527	45	None	As above, plus data system	Limited temp. range
Microsensor Technology Model 203	$7,900	720 (est)	20 (est)	None	Very high speed analysis	No heated sample inlet
Shimadzu Mini-2	$5,000	1552	38	6-10W at 115 vac	Full laboratory capability	AC required. Limited detectors (FIP,ECD)
AID Model 511	$8-9,000	2964	40	None	As above plus good selection of detectors	Limited temp. range
AID Model 210	$6-7,000	1978	32	None	Portable, rugged	Limited temp. range
Baseline 1030A	$15,000	1519	20	100W 110 vac	Rugged, good detector selection	High power consumption
HNU Model 321	$8,000	1586	25	110Vac for temp. programming, injector and detector heating, and ECD use.	Small & inexpensive	Needs AC for useful operation
HNU Model 301P	$7,000	1586	25	110Vac for injector and oven heating, ECD use.	Small & inexpensive	Needs AC for useful operation

*All gas chromatographs will require compressed gases. The number and individual amounts will depend on the detectors used.

Table B-7

Comparison of Fieldable Mass Spectrometers

Instrument	Approximate Cost	Size (in^3)	Weight (lb)	Support Required	Strengths	Liabilities
Bruker MM-1	$200K	20196	319	24V Batteries	Rugged, High sensitivity, MS selectivity	Expensive, Bulky
VG Instruments	$80K	10070	154	24V for air & VOC analysis; AC (generator) for water analysis	Rugged, High sensitivity MS selectivity	Moderately expensive,
Glow Discharge/ITMS	<$200K	?	?	115Vac	Simple, rugged,	Not commercially available

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