Waste Testing and Quality Assurance

Second Volume

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ASTM STP 1062

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ASTM
1916 Race Street
Philadelphia, PA 19103

ISBN: 0-8031-1293-9
PCN: 0-010620-56

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Printed in Ann Arbor, MI
May 1990

Foreword

This publication is one in a continuing series of ASTM monographs on one of the most diverse and far reaching branches of environmental testing—namely that dealing with waste management. The papers presented in this STP series, are an outgrowth of those presented at the annual Waste Testing and Quality Assurance symposium sponsored by the United States Environmental Protection Agency's Office of Solid Waste and Emergency Response. The editor, David Friedman of EPA, serves as symposium chairperson and is the editor of this monograph series. This publication is the second in the series which began in 1988 with STP 999.

Contents

This monograph highlights recent developments in the areas of waste and environmental media sampling, property and hazard assessment, and chemical and biological analysis. It focuses on recent developments in estimating migration of hazardous constituents from wastes, analytical methods development and evaluation, laboratory data management, and quality assurance. While the research and ideas presented in these papers represent studies undertaken to implement the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Monitoring Response, Compensation, and Liability Act (CERCLA) hazardous waste management programs, the methodology and practices are applicable to all forms of environmental monitoring and material characterization.

Air and Ground Water Monitoring

Facilities managing hazardous waste are designed to reduce and, if possible, eliminate release of toxic chemicals to the environment. However, engineering and procedural controls can fail. Monitoring of the environment is therefore undertaken to identify if failure of the containment mechanism has occurred. In addition, monitoring is performed to determine if a site is contaminated, to determine the magnitude of the risk posed by the contamination, to monitor the progress of remediation efforts, and to insure that proper remediation has taken place.

The magnitude of the nation's monitoring effort requires not only that the methods be accurate and sensitive, but that be as cost-effective as possible. Pruskin, in his paper compares and contrasts the use of Total Organic Halogen (TOX)(SW-846 Method 9020) and conventional Gas Chromatography with Mass Spectrometry Detection (GC/MS) (SW-846 Methods 8240 and 8270) as a means of monitoring ground water for contamination. Comparison of Method 9020 TOX values with calculated TOX by GC/MS showed that using GC/MS as an indicator of the presence and concentration of organohalogen underestimates the level of contamination. The author's hypothesis that the additional contamination is due to compounds not amenable to gas chromatography. This is consistent with observations made by many others that conventional analytical methods can only identify a small portion of the total organic materials present in

Monitoring data can only be as good as the sample is representive. In ground water monitoring, sample quality can be adversely affected by improper well construction and operation. Since the well casing is in direct contact with the water to be sampled, if the casing material either sorbs materials from the water or leaches materials into the water the composition of the sample will cease to be representive of the ground water. In his review of the available literature, Dowd analyzes the results of laboratory and field studies so that informed judgments concerning appropriate selection of casing materials can be made. The authors conclusion that there is no significant difference between many of the common casing materials is an important and unexpected finding.

In order to effectively protect public health and the environment it is important for regulatory Agencies and the scientific community to be constantly on the lookout for new sources and types of environmental contaminants. In analyzing their ground water monitoring data the Nassau County, New York Department of Health, Moon and coworkers have uncovered contamination trends that are likely to be of national importance. Their findings of bromoform and other volatile organochlorine species characteristic of those formed during chlorination of drinking water, may indicate a hiterto unexpected route of ground water contamination.

Until the mid 1980s both public and regulatory concern in the hazardous waste program centered on the human health impacts of exposure to contaminated ground water and soils. Little attention was given to the air route of exposure either during waste management or site remediation. As a consequence, analytical methodology for monitoring ambient air for the presence of toxic organic constituents has not received the attention that water and soil testing has. In order to protect the health of workers cleaning up contaminated sites and of persons living in the vicinity of waste management operations, this is changing. Because the concentrations of the compounds of interest are extremely low, matrix interferences pose a major problem. In their paper, Fairless et. al., discuss their application of a new gas chromatographic, matrix isolation procedure coupled with Fourier transform infrared spectroscopy to the problem of ambient air monitoring. While much work still remains, the technique has been shown to provide reliable qualitative and quantitative identification of airborne organic contaminants.

A different approach to determining the presence and concentration of volatile organics in ambient air is described by Wise and Guerin. They describe a new low pressure glow discharge mass spectroscopic method for direct sampling and analysis of volatile organics which eliminates the need for membranes, splitters, or restrictors. The technique offers further advantages of fast analysis (2-3 minutes) and high sample throughput (10 + samples per hour). Early studies indicate that the method can be used to quantitatively measure volatile organics such as benzene, or trichloroethylene at the low ppb level.

Use of canister based sampling for volatile organics has recently undergone a resurgence due to problems experienced with use of solid adsorbents such as Tenax. With the increased availability of electronic flow controllers, constant sampling rates can be maintained for over 24 hours. With the growth being experienced in ambient air sampling and analysis due to regulatory pressures and concerns with worker exposure, it is likely that canister use will increase. In order to ensure that the monitoring data accurately represents air quality, careful selection of a sampling method is critical. In their paper, McClenny and Pleil examine the status of canister based ambient air sampling and discuss some of the tradeoffs in the use of canisters vs solid sorbent sampling.

Biological Test Methods

Environmental monitoring has historically employed chemical analysis to identify instances of environmental contamination and to assess the impact of such contamination. Chemical analysis, however, is severely limited. Using chemical analysis, we can neither analyze for all the toxicologically active materials that are present in wastes, nor can we adequately predict the impact on human health or the environment of the complex mixtures found in the real world. As a result, monitoring using biological test methods is being explored as an alternative to conventional approaches.

In the section on biological test methods, we have brought together a number of papers reporting the results of studies to develop and apply new bioassay based test methods to this problem.

Exposure to genotoxic agents can result in a number of adverse health effects; among the more serious being cancer and birth defects. Since the pioneering research

of Bruce Ames in the early 70's, a great many short-term, in-vitro test systems have become available for evaluating the genotoxic potential of environmental chemicals. Because of the serious nature of the adverse consequences that can result from exposure to genotoxic agents, development of bioassay approaches to evaluating the genotoxic potential of wastes is of great interest and urgency.

The diversity of efforts that are underway and the progress being made is illustrated by the papers by Houk, Sandhu, Lower, and Wang. The salmonella assay developed by Ames in 1975 has been used more than any other short-term assay for determining the genotoxicity of complex mixtures. However, the salmonella assay is known to be relatively insensitive to certain carcinogenic metals, chlorinated compounds, solvents, etc. In order to overcome its limitations, researchers have been developing and applying alternative approaches to studying complex mixtures characteristic of industrial wastes. Houk, et.al., discusses the use of the microscreen phage-induction assay to identify wastes exhibiting genotoxic activity. While Houk employed the phage-induction assay to measure genotoxic activity, Sandhu emphasized use of simple, inexpensive, rapid plant test systems to evaluate the mutagenicity of complex environmental mixtures including coal and wood combustion extracts, industrial effluents, and sludges. The significance of the use of short-term plant bioassays for environmental assays is also discussed.

The Environmental Protection Agency has developed procedures to simulate the leachate that would form from wastes placed in various types of landfill environments. Some of these test procedures contain significant amounts of acetate ion which has the potential to interfere with bioassay evaluation of the simulated leachates. Peterson, et. al. looked at how the choice of extraction fluid impacts the apparent bioactivity of the simulated leachates. Their study explored the difference in bioactivity of leachates derived from both municipal refuse and industrial wastes using both water and the sodium acetate buffer used in EPA Method 1311 (TCLP).

While the above efforts have revolved around development of assays suitable for laboratory use in evaluating environmental samples, interest has been rising in assessing the effects of environmental contamination under real world conditions. The methods of evaluating the induced biological effects on a site to be evaluated is termed in-situ assessment. With in

-situ assays the indicator organisms are introduced to or naturally present at the site and data are collected on effects after actual on-site exposures. Lower, et.al., look at the utility of various assay systems for detecting environmental pollutants in a field situation and review their applicability.

While most of the work conducted to date on short-term bioassays has dealt with the development of more sensitive, selective, faster, or general assays. Before such assays can be used for routine environmental monitoring purposes, it is critical that they be standardized and made rugged. Without such standardization, comparison of data collected from different sites, by different investigators, or at different times is impossible. In addition, standardized methods are needed before regulatory agencies can establish action levels. As Wang, et. al. report, EPA has undertaken significant efforts to develop rugged, standardized protocols for some of the more popular assays.

Leaching and Physical Methods

One of the greatest dangers posed by improper management of hazardous wastes is contamination of ground water. In order to protect the Nation's ground water resources, disposal of wastes which have a propensity to leach toxic species are required to be managed in a way that is protective of human health and the environment. These procedures include treatment before disposal to minimize toxic leachate formation, and disposal in a controlled landfill environment. In a continuation of its program to develop accurate, cost-effective, testing protocols to predict the propensity of a waste to leach, the Environmental Protection Agency developed the Toxicity Characteristic Leaching Procedure (EPA Method 1311). Method 1311, also known as the TCLP, is designed to model the leaching behavior of industrial waste placed in a sanitary landfill environment. In 1986, Method 1311 was proposed both as a replacement for the currently used Extraction Procedure (EPA Method 1310) used in identifying hazardous wastes and for use in the Land Disposal Restrictions Program as a means of determining treatment effectiveness.

Given its broad applicability, a number of studies have been carried out to better understand the behavior of Method 1311 as applied to a wide variety of wastes. In this issue, we have included several papers reporting on the results of such studies. In his review, Newcomer, et. al., summarizes the results of

eight studies conducted to evaluate Method 1311. The study results indicate that the TCLP procedure can be consistently applied by a diverse group of laboratories.

Stabilization of metal bearing wastes is a popular and effective means of treating wastes prior to land disposal. One of the more common stabilization agents is portland cement. Its cementitious properties and alkalinity work in concert to reduce the mobility of many cations. To insure uniformity in testing, Method 1311 requires, even monolithic, materials be prepared by grinding or cutting such that the waste passes through a 9.5 mm standard sieve. No minimum particle size, however, is specified. Prange and coworkers examined the impact waste particle size has on leachability with respect to the mobility of arsenic and chromium. While one might assume that the higher surface area of small particles would tend to increase mobility, Prange found this not always to be the case.

Leaking underground storage tanks have become a national concern. Loss of material, especially petroleum products, poses a risk of ground water contamination and loss of valuable drinking water supplies. Many such petroleum products contain toxic, volatile, highly mobile constituents. In their studies, Romeu and coworkers employed Method 1311 to determine the migration potential of soil contaminated with various petroleum products. The authors found that leachability was a function of both the type of soil and the type of petroleum product.

Metals and Miscellaneous Analytes

While analytical techniques for elemental analytes are quite well developed, the application of many of the techniques to the wide variety of matrices encountered in waste testing raises many questions. As part of the continuing effort to better document the performance of commonly employed methods, studies conducted on both the cold-vapor techniques for mercury (EPA Methods 7470 an 7471) and on Inductively Coupled Plasma spectroscopy (EPA Method 6010) are presented.

Beckert, et.al., studied the cold-vapor atomic absorption methods for mercury (EPA Methods 7470 and 7471) on aqueous systems and solid matrices respectively to determine their sensitivity and precision. Difficulties were encountered when analyzing low level samples and the authors detail the changes developed to overcome the method limitations.

As a consequence of the need to monitor for an ever increasing number of elements, use of multi-element measurement techniques has become prevalent. One of the more widespread of these techniques is Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP). Hinners, et. al,. focuses on the application of Method 6010 to the analysis of complex matrices characteristic of those found when dealing with waste and environmental media such as soils. Since, preparation of the sample by digestion is normally required, a study of EPA Method 3050 was conducted. In their collaborative study the authors determined the accuracy and precision of methods 3050 and 6010 and identify potential problem areas to which an analyst should be sensitive to if ICP is selected as the method of choice.

The use of microwave energy as an alternative to conventional hot plate digestion has been the subject of considerable attention and research interest. Advantages of microwave digestion include reduced preparation time, more efficient digestion, and reduced loss of the volatile elements. The two papers by Binstock and his coworkers, review the results of their studies conducted to evaluate the microwave digestion technique for use with solid matrices characteristic of those encountered in the waste management program. The studies looked at the effect of various parameters and conditions including: acid matrix, heating time, and digestion vessel pressure. Validation of the method was conducted using a variety of matrices including soils, sediments, ashes, and oils.

The ultimate solution to the Nation's hazardous and solid waste disposal problems lies in minimizing the amount of waste generated. One means of minimizing the amount of waste generated is to reuse process residues as either feed stocks or fuels. One opportunity for reusing waste oil as fuel is in industrial and commercial boilers. Since such boilers are often not equipped to handle hazardous wastes, it is important to monitor the properties of the wastes that are used. Due to both the toxicity and the difficulty encountered in destroying halogenated organics, the Environmental Protection Agency has established total organic halogen standards for waste oils that are used as fuels. Accurate measurement of organic halogen content in waste oils has, therefore, received a great deal of attention.

This issue, includes three papers that both indicate the current state-of-the-art in organohalogen measurement as well as demonstrating the progress still being made. Gaskill reports on the results of a

collaborative study to evaluate a number of commercially available, commonly used test methods, while Minucci and Lieu report on new methodology. Lieu studied the performance and advantages of a laboratory pyrolysis/microcoulometric method for determining total organic halides, and Minucci evaluated a portable test kit that can be used for real time analyses in the field.

The cyanide anion is one of the more important yet hard to analyze species encountered by those having to characterize waste properties. Understanding both the definitions and chemistry of the various types of "cyanide" species is critical to accurate measurement and interpretation of the results. In his paper titled "Sample Handling for the Analysis of Cyanides in Solid and Hazardous Waste", Ritzert reviews the cyanide forms of environmental significance and discusses, and illustrates, real world problems associated with the handling, analysis, and interpretation of results.

Organic Analytes

Every year, tens of thousands of environmental samples are analyzed for a wide variety of organic constituents. The amount of testing grows larger every year as new laws are issued, new regulations are promulgated, and business and social concerns sensitize everyone to the dangers of environmental pollution. In addition to the large number of analyses performed, samples often have to be tested for a great many potentially hazardous compounds. For example, the RCRA Appendix VIII list of toxic chemicals contains over 200 organic compounds. As diverse as the universe of constituents of concern is, it is growing every year. Growth is fueled both by the new toxicological information that is becoming available, as well as new developments in analytical chemistry. Our testing methodology has kept improving in order to meet these demands.

In the papers that have been included in this issue, we will highlight several new developments in organic analysis. These developments report and discuss efforts both to make testing more cost-effective, e.g., simpler, faster, less labor intensive, as well as to expand our ability to analyze for additional constituents of human health and environmental concern.

When dealing with the complex matrices characteristic of waste samples and contaminated media, interferences are often encountered when using gas

chromatography. Even using mass spectroscopy, which can often differentiate between the compound of interest and the interferent, there are frequent problems. One approach to solving these problems has been the development of higher performance separation techniques. In their paper, Clark and coworkers compare the higher separation performance of the capillary column methods with the older packed column methods. In addition, the authors compare and contrast the performance and quality assurance requirements for the different gas chromatographic methods used in the solid waste, drinking water, and waste water regulatory programs administered by EPA.

While significant progress continues to be made in the area of gas chromatography, major changes in environmental monitoring are occurring as a result of new developments in high performance liquid chromatography (HPLC). Without having the volatility limitations of gas chromatography, HPLC has the potential to permit one to measure many of the more polar or higher molecular weight compounds of concern. Research highlighted in this issue deals with developments both in derivitization to improve the response of conventional liquid chromatographic detectors and in new interfaces to permit use of the powerful mass spectroscopic detector with HPLC.

Bicking reports on the development and single-laboratory validation of a new derivitization method which permits low level (<10 ppb) analysis of formaldehyde in a water matrix. The method appears to measure only free formaldehyde and formation of formaldehyde, from precursors, during the analysis does not appear to be a problem. This work is important due both the widespread use and concern over the presence of formaldehyde in the environment, and the potential applicability of the derivitization technique to other difficult to analyze carbonyl compounds.

Early attempts to use the mass spectrometer as a detector in liquid chromatography suffered from many problems. Among these were the inability of the interface between the HPLC and the mass spectrometer to handle compounds which were either thermally labile or non-volatile. In the second paper on new developments in HPLC, Apffel examines the recently developed Thermospray and Particle Beam interfaces and compares their applicability and performance for various applications. Guidelines are also presented for selecting between the two techniques for a given problem.

As a consequence of the increased concern with disposal of mixed hazardous and radioactive wastes, increased attention is being given to the difficulties of sampling and analyzing such wastes. In their paper, Tomkins and Caton discuss the problems inherent in characterizing mixed wastes and present approaches and methodology for addressing this increasingly important problem. The methodology described permits the separation of the organic constituents of concern from the radionuclides so that the resulting extracts can be handled in conventional laboratories.

Many state and federal environmental regulatory programs deal with problems caused by petroleum products. In many cases, the needed analytical methodology for carrying out testing and monitoring under these programs has not been codified. In order to consistently achieve the objectives of the New Jersey regulatory programs, the NJ Department of Environmental Protection developed a "Manual of Petroleum Product Analyses" for use by all State of New Jersey regulatory programs.
In their report, Stainken and Miller describe the approach used to develop the manual and discuss the methods that were selected for inclusion. The methods selected are described and references given.

Quality Assurance

Remediation of contaminated sites is a complex and difficult process. If data of sufficient quality is not available to the decision maker, or if incorrect data is used, the potential for error increases substantially. Such errors can have serious health, environmental, and economic consequences. It is, therefore, important that all persons responsible for environmental data gathering efforts ensure that the effort has a quality assurance/quality control program to document the quality of the resulting data.

As a means of ensuring data quality, careful review of all laboratory results is a critical phase of laboratory quality assurance. Data validation is often the rate limiting step in the sampling and analysis process. In order to overcome this potential bottleneck, and to reduce the need for large numbers of skilled staff, the EPA has developed a computerized data validation system to take over some of the more routine aspects of the process. This system, designated RADAS (Regional Automated data Auditing System) determines the validity of individual analyte concentrations by examining protocol mandated factors such as instrument

calibration, sample holding time, and blank levels. Shumann et. al., describes the RADAS system and describes how it has been found by EPA to perform appropriately and give a significant improvement in analysis turn around time.

The Oak Ridge national Laboratory serves as the Quality Assurance Office for a number of Federal Installation Restoration Programs. In their paper, Miller and her coworkers, describe the Quality Assurance/Quality Control programs they employ. The program described is designed to meet the requirements of both EPA's RCRA and CERCLA (Superfund) programs. The approaches presented are applicable to remediation programs conducted by both private and public sector organizations.

Laboratory Information Management

The computerization of laboratory instrumentation and the use of automated sampling and data management systems has greatly increased the rate of data generation. The consolidation of this data into a manageable form that can be reviewed and used by the decision maker has not progressed as rapidly. Automation of the data consolidation process offers the laboratory an important area for significant productivity gains. In addition, automation of this aspect of the monitoring process can significantly reduce the level of transcription errors when laboratory data reports are prepared. Low examined how personal computers can be used in conjunction with laboratory data systems to improve the consolidation process.

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ISBN 0-8031-1293-9