UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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MEMORANDUM # 36

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SUBJECT: Notes on RCRA Methods and QA Activities

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This memo addresses the following topics:

- 1992 Symposium on Waste Testing and Quality Assurance
- Issue Discussion Groups
- Inorganic Methods Workgroup Meeting
- Organic Methods Workgroup Meeting
- QA Workgroup Meeting
- Miscellaneous Methods Workgroup Meeting
- ICP Discussion Group
- HPLC Methods Discussion Group
- SPA Methods Discussion Group
- SFE Methods Discussion Group
- SW-846 Update and TCLP Spike Recovery Correction Removal Notice Update
- Total Analysis Versus TCLP.

1992 Symposium on Waste Testing and Quality Assurance

The Environmental Protection Agency's Eighth Annual Waste Testing & Quality Assurance Symposium was held on July 13-17, 1992 at the Hyatt Regency Crystal City in Arlington, Virginia. We are extremely pleased at the continued growth of the Symposium with respect to the number of attendees and the quality and scope of the material presented. We would like to thank all presenters, course instructors, and facilitators for making this year's symposium interesting and educational. The EnvirACS exposition was widely attended and provided attendees with the latest technical information on sampling and testing equipment, laboratory instrumentation, and information management systems.

Issue Discussion Groups

This year's program featured four issue workshops offering attendees a unique opportunity to assist the Agency in exploring and evaluating new approaches to solving monitoring issues important to EPA's regulatory programs. Each workshop included an introductory session at which the views and perspectives of the Agency, the regulated community, and the scientific community were presented. After the introduction, each workshop separated into three discussion groups of approximately 75 participants. These discussion groups offered participants an opportunity to voice their ideas, concerns, and suggestions on each of the following issues:

- Issues associated with adoption of performance-based methods;
- Predicting the environmental impact of oily materials;
- Characterizing heterogeneous materials; and
- Characterizing mixed wastes.

We were pleased by the interest shown in these discussion groups and would like to thank all discussion group participants for their valuable ideas and suggestions. We are currently summarizing the notes from these discussion groups and will make them available in the near future.

1) Issues Associated With Adoption of Performance-Based Methods

The Environmental Protection Agency administers a number of regulatory programs that require the collection of high quality environmental data. In the past, the Agency has adopted a policy of promulgating specific test methods for compliance monitoring and testing. The Agency is investigating a new approach to compliance monitoring, one which would focus less on the development of mandatory analytical methods and more on method performance. A performance-based method approach would allow greater flexibility in the selection and/or development of methods as long as certain performance requirements were met.

However, the implementation of this new approach is not easy. Several important issues must be addressed before serious consideration can be given to this new approach. The focus of this discussion group was centered on the following questions.

How will acceptable performance be defined?

What documentation is needed to verity compliance with performance based standards?

The discussion groups commented on four basic methods for defining acceptable performance:

- Accreditation and certification;
- Use of standard quality control;
- Interlaboratory validation/external peer review; and
- Comparison to reference methods.

The first approach would employ a national accreditation or certification program to ensure acceptable method performance. The goal of a national accreditation program would be to ensure a minimum level of laboratory proficiency. This program could be administered by regional EPA offices or through organizations such as the American Chemical Society. Certification would focus on the performance of the laboratory rather than on specific methods. Each laboratory could be certified for specific analytical tests such as volatile organics or PCBs. Key components of the certification process would include an auditing system to provide oversight on laboratory performance, accreditation and validation of laboratory protocols, quality control procedures, and defined documentation procedures.

Nearly all participants voiced support for the use of standard quality control as an effective means of demonstrating acceptable method performance. A sound laboratory QA/QC program is essential in assuring acceptable performance. Using this approach, the laboratory would be given the freedom to select the best method for the analytical task at hand. As long as certain well-defined quality control standards were achieved, any method could be employed. Blanks, matrix spikes, matrix spike duplicates, reference materials, and blind QC samples were cited by the discussion groups members as key elements in documenting method performance. Several participants suggested that the Agency should establish minimum quality control guidelines for each of these elements while other participants suggested that a project-specific quality assurance project plan (QAPjP) should be the driving force behind minimum quality control requirements. Using a QAPjP approach, each project could define data quality in accordance with specific data quality objectives.

Several participants recommended that a system of interlaboratory validation studies should be used to validate performance-based methods. These studies would be performed on the actual sample matrix for which the method was developed to fully access accuracy, precision, and ruggedness of the method. Other participants were concerned with the timeliness and cost of such a program. In a related suggestion, another participant suggested that a peer review process could be used to assess method performance and could involve both the Agency and the regulated community.

Many people supported the use of reference methods as an important means of assessing acceptable performance based methods. In general, the ability of a new or modified method to generate statistically equivalent data as compared to a standard or reference method would prove acceptable performance. Many participants agreed with this concept, but noted limitations with respect to the absence of performance data for some methods and the absence of standard methods for certain difficult matrices.

A number of suggestions were made regarding documentation requirements. Some participants were in favor of global documentation requirements such as GLP or ISO standards. Most participants thought that documentation requirements should be defined in advance in a QAPjP in accordance with the project DQOs. Documentation requirements could be project specific and commensurate with the complexity of the project. All participants agreed that the results of standard quality control samples would be an important element in documenting acceptable performance.

2) Predicting the Environmental Impact of Oily Materials

Oily wastes are a major concern to the Agency due to their enormous volume and to their potential to inflict environmental damage, especially with respect to groundwater contamination. Over the years, the Agency has developed test methods, fate and transport models, and regulatory standards to manage wastes that pose a threat to groundwater. Test methods, including EPA methods 1310 (EP), 1311 (TCLP), and 1330 (OWEP), have been developed to predict the toxicity of various wastes buried in a landfill. Unfortunately, all of these procedures have deficiencies with respect to predicting the mobility of toxicants from oily wastes. Given the impact on oily wastes on the environment, it is important that new methods be developed that can accurately and precisely predict the movement of oily waste contaminants.

The focus of the oily waste discussion group centered on the following question:

What would be the best approach to use to predict the nature and concentration of the components that would leach from an oily waste if the waste were placed in an unlined landfill?

A number of commenters noted that the universe of oily wastes is extremely complex with respect to physical and chemical properties. Before a discussion can be made on the methods for predicting the mobility of contaminants from an oily waste, the Agency should first define and classify the universe of oily wastes. One commenter suggested a classification system based upon the physical properties of the waste, such as density and viscosity. Another system would focus on a process-related approach based on the oily waste generator (i.e., tanning wastes, petroleum refining wastes, slaughter house wastes, and metal working sludges). One participant recommended that a survey of oily waste generators may be useful in developing a classification system for oily wastes and could also provide useful data on the amounts, type, and current disposal practices of oily wastes.

A number of important points were made concerning the various testing options available for assessing the oily waste impact on the environment. Among the issues discussed, two basic criteria emerged for leachability testing:

- The test(s) must address the problematic technical and procedural issues dealing with oily wastes. The procedural problems in applying the TCLP to oily waste were frequently cited as the type of difficulties that must be specifically addressed. Difficulties in estimating percent solids, premature filter clogging, and emulsion formation were some of the problems cited with the TCLP.

- The test(s) should be representative of the actual disposal conditions of a landfill with respect to soil type, particle size, rainfall amount, and leachate characteristics. Secondly, the test must closely model the movement and transport mechanisms of oily wastes in the environment.

Testing Approaches:

Multi-Test Approach

A number of participants supported the concept of a multi-test approach for evaluating the impact of oily materials on the environment. Given the diverse universe of "oily wastes," a single "best" leaching test may not be feasible or scientifically valid. In a related suggestion, a "generic" testing protocol could be developed with certain built-in testing variables. These variables may include the volume and composition (including pH) of leaching fluids, the nature of soil types and particle size, and flow rates. In addition, the leaching tests could be made "site specific" by employing native soils and leaching fluids, thereby more accurately predicting the toxicity of the waste under real-world conditions.

Several commenters recommended a tiered approach for oily waste testing. Using this approach, the waste would first be tested by the most conservative or aggressive test, such as a compositional analysis. If the initial tests demonstrated that the waste was not hazardous, no further testing would be required. If the initial test demonstrated that the waste was potentially hazardous, less conservative tests could be applied in a step-wise fashion to characterize the waste, ending in actual laboratory leaching tests. In a closely related suggestion, a "quick and dirty" screening procedure could be developed to screen oily wastes. Wastes that are identified as potentially toxic could then be tested using more elaborate leaching tests.

Column Leaching Technique

Many discussion participants expressed support for the development of a column leaching technique as the best method for simulating the real-world movement and transport of oily wastes in the environment. In addition to eliminating some of the procedural problems associated with the TCLP, a column leaching procedure could be made site-specific by incorporating native soils and leachates. One commenter noted that liquid or semi-liquid oily waste could be immobilized by adding inert materials to the column. This would aid in keeping the oily material in the column and would increase permeability and extraction efficiency.

A number of participants suggested that further research was needed to fully evaluate a column leaching method for oily wastes. Test variables should be ranked in order of importance, and research efforts should be focused on these issues. These issues include the nature and type of column substrate (i.e., soil type, particle size and percent moisture), leaching fluid (s) composition, flow rates, etc.

Mathematical Model

Several discussion participants supported the concept of a mathematical model for predicting the nature and composition of components leaching from a landfilled oily waste.

One commenter suggested that each oily waste could be characterized through physical testing. This information could then be plugged into a mathematical model to predict the relative toxicity of the waste. In general, a mathematical model must incorporate dilution attenuation factors, partition coefficients, toxicity data, and any other significant variables. The model also should consider regional and geographical differences in soils and rainfall characteristics. Finally, the mathematical model must be validated against actual real-world data to assure that it accurately predicts the toxicity of oily wastes.

3) Characterizing Mixed Wastes:

Hazardous waste characterization and management of Mixed Waste presents a unique challenge to the Agency and the regulated community. Accurate characterization of a mixed waste is required to determine if and/or how the waste will be managed under RCRA. Much of hazardous waste characterization is performed by actual testing of the waste. Meeting RCRA testing requirements is complicated by the presence of radionuclides in mixed wastes, which present additional handling and safety considerations beyond that of non-radioactive wastes. In addition to these concerns, management options for mixed wastes are limited and costly.

The purpose of this discussion group was to formulate ideas and suggestions on the best way to characterize mixed wastes. Two central questions were presented to each discussion group:

What kind of information is needed (what quantity and quality) to safely manage mixed wastes for a series of waste management options? In a related question;

What scientific properties or constituents of mixed waste should be determined?

Each discussion group developed a list of important information regarding safe handling of mixed wastes for the various management options. The management options discussed included: entombment in a below-ground cavern, incineration, solidification, vitrification, reinjection, transmutation, and interim warehouse storage.

Entombment

Safe handling of mixed waste by entombment first requires physical separation of the waste based on physical matrix or waste type (i.e. sludge, filter cake, clothing, etc.). This information may be obtained through process knowledge or direct physical testing. Free liquid, either as a component of the waste or at the disposal site must be chemically or physically removed prior to placement. The potential generation of leaching fluids by infiltration of rainwater/groundwater must be considered. In addition, compatibility information for different waste types must be evaluated. Mixing of incompatible wastes during transports, placement, or during long-term storage may result in adverse reactions including gas production, heat generation, and the production of highly toxic contaminants. These issues must be considered in the short term (i.e., during storage, transport, and placement) and in the long term (i.e., when waste containers disintegrate or when burial chambers collapse).

The radioactive properties of the waste(s) also must be known, including the formation of daughter products. Heat generation from the decay of mixed wastes could have important ramifications concerning the mobility of contaminants from the waste and the generation of toxic gases.

Several participants noted that the TCLP was an inappropriate test for entombed waste. According to these commenters, the TCLP does not accurately model the actual burial condition's of an entombed mixed waste, especially those mixed wastes buried in salt domes. In addition, because no salt migration has occurred at these sites for thousands of years, leaching tests were not necessary. If leaching tests are mandated, a brine leachate should be incorporated into the test.

Incineration

Prior to incineration, the waste must be evaluated for its physical properties, including physical form, BTU value, moisture and ash content, viscosity, and flashpoint. These waste characteristics will have a direct impact on how the wastes will be incinerated with respect to feed rates, operating conditions, and incineration temperatures.

Many discussion group members noted that the chemical content of the mixed waste must be evaluated. Among the chemicals cited were mercury, lead, PCBs (especially tri- and tetra-chlorobiphenyls as they are precursors to dioxins), total halogen content (as an indicator of halogenated solvents), total sulfur, NO_x, and volatile radionuclides (i.e., H-3, C-l4). Several participants noted that the public would demand the monitoring of all possible air contaminants covered under the Clean Air Act. It was suggested that a list of specific target analytes should be developed for mixed wastes in order to minimize testing costs. It also was suggested that air quality monitoring should be made a part of the permit process.

The radioactive properties of the waste also must be identified, including the specific activity of the waste from gross alpha, beta, and gamma measurements.

One workgroup discussed other issues associated with waste incineration. It was suggested that potentially expensive characterization analysis, such as those for volatile radionuclides and PCBs, could be eliminated by applying process knowledge. Alternative methodologies that are better, faster, and cheaper may become available. Risk of population exposure around incineration operations and DOT shipping regulations also may impact on the characterization requirements of the mixed waste and incineration residues.

Solidification

The most important considerations for solidification of mixed wastes include setting time, compaction strength, heat generation, leachability, and stability of the stabilization product. These factors are critical when evaluating the long-term physical and chemical stability of the solidified waste product.

The total organic content of the mixed waste should be evaluated because the presence of organic materials may interfere with the solidification process, resulting in lower compaction strength, greater leachability, and eventual loss of physical integrity. In addition, the presence of volatile organic compounds (VOC) may present a safety hazard to workers during the curing and placement stages of the process. The total anion content of the waste also must be evaluated as a high level of anions may prevent stabilization or adversely affect the strength of the product.

One possible testing approach was suggested to ensure that solidification was performed in a safe and cost effective manner. It was proposed to test and evaluate the solidification product for compaction strength, leachability, and physical stability. If the solidification product fails any of these tests (i.e., fails to set or leaches toxic constituents), then a detailed chemical analysis should be performed on the waste. If the product passes the criteria for strength, stability, and leachability, then costly chemical analysis need not be performed.

Other Waste Management Options

Other waste management options were briefly discussed. Vitrification was cited as the best technology for managing mixed wastes in terms of cost and safety, and requires the least amount of waste characterization. Developmental costs may be high before this technology can be fully implemented.

Deep-well injection also was suggested, and would require waste characterization similar to that required for entombment.

Transmutation of actinides and fission products to stable or short-lived species may be a practical solution and may not cost much more than waste characterization.

It was suggested that interim warehouse drum storage may be the best short-term solution for managing mixed wastes until we better understand the complexities of mixed wastes and further evaluate alternative management options.

4) Characterizing Heterogeneous Materials

Characterization of a solid waste is essential for determining whether a waste is hazardous or for developing management and treatment standards for hazardous materials. Current EPA regulations for characterizing waste includes determining the average property of the "universe or whole." This task is difficult when applied to heterogeneous wastes because conventional sampling and compositing techniques are often inadequate in providing a "representative sample" of the waste. As a result, analytical results are often biased and imprecise, making compliance decisions difficult.

The purpose of this discussion group was to formulate ideas and suggestions on the best way to characterize heterogeneous wastes. Two central questions were presented to each discussion group:

Should EPA change from the current practice (average testing) to attribute testing far properties that are not averageable? If so, what is the highest practical degree of confidence (%) that could be required?

Several discussion group members expressed concern over the sampling techniques employed for both average and attribute testing. Faulty sampling techniques may account for up to 80% of the errors associated with data comparability. The groups suggested that EPA adopt specific guidance through cooperative efforts with other public and private agencies for sampling heterogeneous wastes.

The issue of "hot spot" identification was discussed at length. "Hot spot" identification was probably the most effective means to minimize the volume of heterogeneous waste. This could be accomplished by identifying "hot spots" within the waste stream either through process knowledge of the waste or by extensive field screening. It was suggested that "hot spots" could potentially be segregated and thereby minimize the volume of heterogeneous hazardous waste. The Agency was encouraged to develop guidelines for generators to segregate non-compatible hazardous waste.

Attribute testing was briefly discussed. The general consensus was that attribute testing was probably the most costly testing option because of the need to analyze every sampling point and each strata within the waste. Other participants noted that average testing could be used to characterize a heterogeneous waste by collecting a number of samples and compositing them to generate a single data point. Nearly all participants agreed that flexibility was desirable and that the Agency should develop specific guidance for defining the situations where attribute or average testing are most appropriate.

Several participants recommended a hierarchical approach to heterogeneous waste management. This approach would be articulated in a site-specific QAPjP using site-specific DQO's. The goal of the hierarchical approach would be to categorize the extent of hazardous waste contamination based on strata and health based criteria for each waste constituent identified. The decision to remediate a site would therefore depend on the risk factors associated with each stratum identified within a heterogeneous waste.

Only a few comments were made concerning the percentage or degree of confidence that could be required for attribute testing. The difficulty with assigning a percentage was that this was perceived to be site-specific. Risk factors would need to be evaluated on a site-specific basis. It was recommended that a percentage must be applied on a sliding scale based on the total volume of heterogeneous waste. For the 65 members that were able to vote, 66% believed that a range of 4 - 6% was reasonable for the percentage allowable for attribute testing.

For additional inquires or comments on these issues, please contact: Mr. David Friedman (RD-680), U.S. Environmental Protection Agency, Washington, D.C. 20460 or call (202) 260-3535.

Workgroup Meetings

The Methods Section Workgroup and Methods Discussion Group Meetings were held in conjunction with the Waste Testing and Quality Assurance Symposium. The following is a brief summary of the topics discussed in each workgroup meeting.

Inorganic Methods Workgroup Meeting

The Inorganic workgroup meeting was led by Ollie Fordham of the Methods Section of the Office of Solid Waste. The workgroup meeting provided comments and input on draft Methods 0012 (Determination of Metals In Stack Emissions) and 0013 (Determination of Hexavalent Chromium Emissions From Stationary Sources). These methods will be incorporated into SW-846 for the purpose of monitoring metal emissions from hazardous waste incineration.

A suggestion was made to include the use of a standard reference material to Methods 3040 (Dissolution Procedure for Oils, Greases, or Waxes) and 3051 (Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils). SRM 1085, "Wear Metals in Oils" was recommended for this purpose.

Method 6010B (ICP) was discussed at length, and it was agreed that portions of the EMMC method dealing with QC and linearity would be incorporated into future updates of Method 6010.

Ed Heithmar of EMSL-LV provided an overview of the ion chromatography methods. Method 6060 (Ion Chromatography of Trace Metals) has undergone a single laboratory validation study and the results will be added to the method. Method 9--- (Chemically Suppressed Ion Chromatography) needs a multi-laboratory validation before additional development of the method can be pursued. A method number has not been assigned to this method, but it will be included in the 9000 series methods.

The workgroup also discussed Method 3060 (Alkaline Digestion/Hexavalent Chromium). This method was included in the Second Edition of SW-846, but was deleted from the Third Edition and its First Update due to poor method performance. It was decided that additional work on this method is needed before a viable procedure can be proposed.

Method 7521 (GFAA for Nickel) also was deleted from SW-846 due to potential contamination problems associated with the use of nickel-base matrix modifiers. It was noted that the use of non-nickel modifiers or the use of dedicated instrumentation justified incorporation of this method back into SW-846.

Two new analytical techniques for metals were briefly discussed, Potentiometric Stripping Analysis (PSA) and Ion Selective Electrode (ISE). These methods may be added to SW-846 at some later date, and will be provided as optional test methods.

For further information on the status of any of these methods, please contact Ollie Fordham at (202) 260-4778.

Organic Methods Workgroup Meeting

The SW-846 Organic Methods Workgroup met and reviewed several new and revised methods being considered for inclusion in the Third Update of the Third Edition of SW-846. The Third Update is scheduled for proposal concurrent with the promulgation of the Second Update. Additional new methods approved by the Workground, at this meeting, for potential inclusion in the Third Update package include:

Method 0100: Sampling for Formaldehyde and Other Carbonyl Compounds in Ambient Air

Method 3530: Pesticides and PCBs by Open-Tubular Solid Phase Extraction

Method 3560:* Petroleum Hydrocarbons by Supercritical Fluid Extract ion

Method 3585: Volatile Organics in Oily Matrices by Solvent Dilution/Direct Inject

Method 4010:* Pentachlorophenol (PCP) in Water and Soils by Immunoassay

Method 4020:* Polychlorinated Biphenyls (PCBs) in Soil by Immunoassay

Method 4030:* Total Petroleum Hydrocarbons (TPH) in Soil by Immunoassay

Method 5022: Volatile Organic Compounds in Oil Matrices Using Heated Automated Headspace Apparatus

Method 5031: Non-Purgeable Volatile Organic Compounds by Azeotropic Distillation (including Microdistillation Technique)

Method 5032: Volatile Organic Compounds by Closed System Vacuum Distillation with Cryogenic Condensation

Method 5035: Volatile Organic Compounds in Solid Matrices by the Purge-and-Trap Procedure

Method 8266: Volatile Organic Compounds by Isotope Dilution GC/MS

Method 8276: Semivolatile Organic Compounds by Isotope Dilution GC/MS

Method 8325: HPLC/PB/MS General Method for Benzidines and Related Compounds

Method 8440:* Total Extractable Petroleum Hydrocarbons (TPH) by Infrared (IR) Spectrometry

Method 8510: Field Method for the Determination of RDX, TNT, and 2,4-DNT in Soil (Method 8515 for TNT incorporated)

Method 8520: Continuous Measurement of Formaldehyde in Ambient Air (UV/Vis)

Draft copies of methods marked with an asterisk (*) above are currently available from the Methods Section, and can be obtained by calling the MICE service at 703-821-4789. Draft copies of the other methods will be made available as they are completed over the next several months.

The Workgroup decided that it would be useful to prepare a generic Method 5000 - Preparation of Volatile Analytes similar to Method 8000 - Gas Chromatography. Method 5000 should be part of the Third Update package and will include information on the applicability of the individual VOA preparatory methods to particular analytes. It will also contain actual recovery data for each method from several matrices.

Additionally, Method 8000 was expanded and renamed, as Method 8000B - Chromatography, to include guidance on high performance liquid chromatography (HPLC) as well as GC.

The Workgroup agreed that the use of ion trap GC/MS should be included in the Third Update package. However, whether separate ion trap methods should be prepared or whether ion trap guidance should be incorporated into existing GC/MS methods will be decided later.

For further information on organic methods, please contact Barry Lesnik at (202) 260-7459.

QA Workgroup Meeting

The Quality Assurance Workgroup was chaired by Charles Sellers and Charles Plost. The OMB mandated changes to Chapter One of SW846 were discussed at length. Most of the workgroup participants agreed that changing the quality control requirements of Chapter One from mandatory to guidance was likely to have a detrimental effect on the quality of environmental data. In a related discussion, one workgroup member suggested that the Agency develop a separate document identifying the most important QC elements of Chapter One.

A number of suggestions for revising Chapter One also were raised. Leon Lazarus, EPA Region II QA Officer, recommended that Chapter One be divided into two sections depending on the intended use of the data. One section would deal with routine sampling and analysis applications while the other would specifically address hazardous waste testing. The level of QC required for each application could then be defined.

The re-establishment of the OSW's Performance Evaluation Studies was announced and discussed. The purpose of these new studies will be to provide performance data for newer SW-846 test methods and to compare the performance of revised methods against the original methods. Charles Sellers reviewed a proposed three-year plan for both organic and inorganic performance studies entitled "Solid Waste Intercomparison Samples" (SWICS) with the workgroup members. A request was made by several participants to prioritize the methods to be tested. Several other related issues also were discussed including sample stability and homogeneity and use of performance data.

Llew Williams of EPA EMSL-Las Vegas, announced an interagency committee meeting which was held in Las Vegas on September 15 through 17, 1992. He also presented an idea to hold a half-day meeting to evaluate the level of QC applicable to a series of sampling and analysis scenarios provided by the EPA Regions. The goal of this meeting will be to define and categorize the level of QC appropriate for each sampling scenario.

For information on quality assurance issues, please contact Charles Sellers at (202) 260-3282.

Miscellaneous Methods Workgroup Meeting

The Miscellaneous Methods Workgroup Meeting was led by Kim Kirkland. Following a brief discussion on the status of the First Update Methods, the group discussed the new radiation methods developed by the National Air and Radiation Environmental Laboratory (NAREL). Vicki Lloyd of NAREL noted that her laboratory is working to develop performance data for solid matrices for Method 9334 (Radiochemical Determination of Americium In Ashed Samples) and that the scope of this method will be further defined pending the results of these studies. Commenters also noted that Methods 9338 (Radiochemical Determination of Technetium-99 In Water) and 9340 (Radiochemical Determination of Tritium In Milk. Soil, and Vegetation-Azeotropic Method) needed additional performance data. Method 9341 (Radiochemical Determination of Carbon-14 In Liquid and Solid Samples) needs more work before it can be proposed.

The group discussed whether SW-846 should incorporate detailed instructions for cleaning glassware and for disposing radioactive wastes. Vicki Lloyd noted that laboratories involved in radiochemical testing must be licensed through the NRC, and that these issues probably have been addressed. Additional requirements mandated by the Agency would not be a good idea.

Method 9023 (Extractable Organic Halides) (EOX) was discussed briefly. It was noted that special consideration must be given to cleaning the pyrolysis boats due to the threat of cross- contamination. One commenter noted that the Soxhlet extraction method for extraction of organic halides appeared to be much more efficient than sonication extraction. Method 9012 (Total and Amenable Cyanide-Automated) was discussed and it was suggested that errors in adjusting the pH of the amenable cyanide sample could result in a negative amenable cyanide value. Cathodic Stripping Voltammetry (CVS) methods for cyanide and sulfide were also discussed and it was agreed that they should be incorporated into a future update of SW-846. One participant suggested that the duplicate precision criteria for Method 9020 (Total Organic Carbon) was too stringent and should be changed to 10% RPD. The workgroup may consider this change after further review of the method.

Mr. Rick Corbett of Corrosion Testing Laboratories Inc. led a discussion of Method 1110 (Corrosivity Towards Steel). Mr. Corbett is the NACE task group chairman for general corrosion testing and regularly receives calls from SW-846 users on this method. He noted that corrosion testing was not an exact science and experienced personnel are needed to generate accurate corrosivity data.

He recommended the use of sheet metal when conducting corrosivity testing towards steel, because the sheet metal best represent the form of steel found in barrels. He also noted that sheet metal is approximately 1″x2″x1/8″ thick and comes in rectangular form, which NACE recommends. The rectangular sheet metal would then have to be cut into the shape of a coupon. He pointed out the various types of steel that may be used such as 1018, and 1008. Mr. Corbett also noted that these two types of sheet metal could be used because of their similar cross sectional area.

Method 1110 specifies the use of 1020 steel which is commonly found in round form. However, the Agency has received comments pointing out that 1020 steel is hard to acquire and is very expensive. Most often the 1020 steel is found more readily in bar stock form and not sheet metal. Therefore, the Agency plans to discuss ways to improve the method at the next Miscellaneous workgroup meeting.

For additional information on this topic or any miscellaneous methods, please contact Kim Kirkland at (202) 260-6722.

ICP Discussion Group

The ICP Discussion Group met briefly to review recent developments to Method 6010, Inductively Coupled Plasma Emission Spectroscopy. The meeting was convened by Ollie Fordham of the Methods Section of OSW. Mr. Fordham provided an overview of the method and noted that the method is being revised to incorporate some of the quality control requirements contained in the EMMC ICPAES method.

Ed Heithmar gave a short presentation outlining the Leopard Team's research goals. This team was organized to coordinate research activities among the ORD laboratories. The goals of this group are focused on lowering detection limits, improving data quality, and developing speciation methods.

For more information on Method 6010, please contact Ollie Fordham at (202) 260-4778.

HPLC Methods Discussion Group

On Friday, July 17, the HPLC Discussion Group met to discuss the latest Agency developments in the field of HPLC methods for the analysis of solid waste. Barry Lesnik of the OSW Methods Section chaired the meeting. The chairman began the meeting by stating that the organic Methods Workgroup had approved four new HPLC methods for inclusion in the Update 3 methods package. The four new methods are numbered and titled: Method 8317--MOCA by HPLC; Method 8325--Solvent Extractable Non-volatile Compounds by HPLC/Thermospray/MS; Method 8332--Nitroglycerine by HPLC; and Method 8350--Non-Volatile Aromatic Sulfonic Acids by Anion Exchange HPLC/UV/ Particle Beam/MS.

The meeting continued with brief overviews of the programs at EMSL-Las Vegas and at EMSL-Cincinnati. The EMSL-LV program has been focusing on analyses of carbamates by HPLC/Thermospray/MS and has found that for those compounds with chromophores, UV detection gives better quantitation. Method 8325 has just been finished by EMSL-CI.

Two presentations were given to the group. First, Dr. Af Afghan, from the Canadian Department of the Environment, described his laboratory's instrumentation, capabilities, and general program direction. Second, Chemist Brad Anderson from APPL Laboratories presented a quick summary of the work done to develop an LC/Thermospray/MS technique that would identify and quantitate a set of eight thiocarbamates down to a method detection limit of 0.1 mg/L. Average recoveries of the technique for 32 surface water samples ranged from 67% to 102% and from 65% to 79% for 32 ground water samples.

The meeting ended with an open question and comment session. Questions regarding the HPLC discussion group should be directed to Barry Lesnik at (202) 260-4761.

SPA Methods Discussion Group

The Solid Phase Adsorbents Discussion Group was led by Larry Johnson. Craig Markell of 3M provided a brief overview of last year's meeting and an update on current research efforts. Mr. Markell noted that Chemical Waste Management reported success with Method 608 for groundwater. Preliminary work with Method 8270 and 8080 also has looked promising for groundwater applications. Use of SPA for monitoring herbicides in rainwater also is underway.

A number of participants questioned the purpose and necessity conditioning SPA columns with methanol. The purpose of conditioning the SPA columns with methanol is to activate the adsorbent (i.e., move the C-18 molecules apart so that they can react with solute molecules). Methanol also fills in pores and eliminates air pockets.

After conditioning with methanol, water is then used to keep the adsorbent wet. While the exact function of methanol is not known, methanol conditioned columns have performed significantly better than those cartridges conditioned with water.

The issue of column plugging also was discussed. Generally it was noted that dirty water is not a problem, except in those cases where suspended solids are heavy enough to plug the cartridge. New developments are underway to incorporate a sieve above the sorbent bed to remove larger particles and to reduce column plugging. In a related topic, the merits of the push vs. pull system for filtration were discussed. A pull vacuum system of filtration is limited to 1 atmosphere of pressure, while a push system could exert significantly more pressure.

Contamination of cartridges from phthalates also was discussed. It was agreed that if cartridges are conditioned and stored properly, phthalate contamination is not a major problem. For pesticide analysis, one commenter recommended prewashing the cartridge with the final eluting solvent to remove any phthalates prior to use.

For further information on SPA applications, please contact Barry Lesnik at (202) 260-7459.

SFE Methods Discussion Group

The Supercritical Fluid Extraction (SEE) Discussion Group was chaired by Barry Lesnik. The major topic of discussion was the approval of Method 3560 - Supercritical Fluid Extraction (of Total Petroleum Hydrocarbons) by the SW-846 Organic Methods Workgroup for possible inclusion in the Third Update package. This package will be proposed concurrently with the promulgation of the Second Update, most likely some time in 1994. Draft copies of Method 3560 are now available from the Methods Section, and can be obtained by calling the MICE service at 703-821-4789. Round robin results showed recoveries that compared favorably to those obtained with Freon 113, with good precision.

EMSL-LV was working on an SFE method for phenoxyacid herbicides, while EMSL-Ci was working on an SFE method for extraction of semivolatiles from wastewaters. The proposed EMSL-Ci technique utilizes solid-phase cartridges as a collection substrate to separate the organics from the aqueous phase, followed by SFE of the substrate.

The instrument manufacturers are working with the Agency to determine the optimum SFE conditions for the major classes of semivolatile analytes. This input will help expedite development of a broader scope for Method 3560.

For further information on SFE topics, please contact Barry Lesnik at (202) 260-7459.

SW-846 and TCLP Spike Recovery Correction Removal Notice

The final SW-846 Update I rule and the proposed Update II rule packages are both currently at the Office of Management and Budget (OMB) review step in the regulatory process. It is not known how long this review step will take. Once the review by OMB is complete, it is expected that the promulgation of Update I and the proposal of Update II will take at least 2 months.

The rule to delete the matrix spike correction requirement from the TCLP which was finalized on June 29, 1990, has been published (57 PR 55114-56117, November 24, 1992). This rule withdraws the spike recovery correction requirements from the TCLP and, except for a few technical and format changes made in the June 29, 1990 rule revising the TCLP, returns the QA provisions of the TCLP to those promulgated on March 29, 1990 (55 FR 11796). Specifically, this rule requires the method of standard additions as the quantitation method for metallic contaminants when appropriate as specified in the method.

For further information on SW-846 updates or the TCLP rule, please give Kim Kirkland a call at (202) 260-6722.

Totals Analysis Versus TCLP

Over the past year, the Agency has received a number of questions concerning the issue of total constituent analysis with respect to the TCLP. Section 1.2 of the TCLP allows for a compositional (total) analysis in lieu of the TCLP when the constituent of concern is absent from the waste, or if present, is at such a low concentration that the appropriate regulatory level could not be exceeded. A number of persons have contacted the MICE Service and have requested clarification on this issue with respect to a number of waste testing scenarios.

Wastes that contain less than 0.5% dry solids do not require extraction. The waste, after filtration, is defined as the TCLP extract. The filtered extract is then analyzed and the resulting concentrations are compared directly to the appropriate regulatory concentration

For wastes that are 100% solid as defined by the TCLP, the maximum theoretical leachate concentration can be calculated by dividing the total concentration of the constituent by 20. The dilution factor of 20 reflects the liquid to solid ratio employed in the extraction procedure. This value then can be compared to the appropriate regulatory concentration. If this value is below the regulatory concentration, the TCLP need not be performed. If the value is above the regulatory concentration, the waste may then be subjected to the TCLP to determine its regulatory status.

The same principal applies to wastes that are less than 100% solid (i.e., wastes that have filterable liquid). In this case however, both the liquid and solid portion of the waste are analyzed for total constituency and the results are combined to determine the maximum leachable concentration of the waste. The following equation may be used to calculate this value.

$$\frac{[AxB] + [CxD]}{B + [20\ L/Kg\ x\ D]} = E$$

where: A = concentration of the analyte in liquid portion of the sample (mg/L)

B = Volume of the liquid portion of the sample (L)

C = Concentration of analyte in the solid portion of the sample (mg/kg)

D = Weight of the solid portion of the sample (kg)

E = Maximum theoretical concentration in leachate (mg/L)

To illustrate this point, the following example is provided:

An analyst wishes to determine if a lead processing sludge could fail the TC for lead. The sludge is reported to have a law concentration of lead, and the analyst decides to perform a compositional analysis of the waste instead of a full TCLP evaluation. A representative sample of waste is subjected to a preliminary percent solids determination as described in the TCLP. The percent solids is found to be 75%. Thus, for each 100 grams of this waste filtered, 25 grams of liquid and 75 grams of solid are obtained. It is assumed for the purpose of this calculation that the density of the filterable liquid is equal to one. The liquid and solid portion of the sample are then analyzed for total lead. The following data are generated:

Percent solids = 75%
Concentration of lead in the liquid phase = 0.023 mg/l

Volume of filtered liquid = 0.025 L
Concentration of lead in the solid phase = 85 mg/kg (wet weight)
Weight of the solid phase = 0.075 kg.

The calculated concentration is as follows:

$$\frac{[0.023\text{ mg/L x }0.025\text{L}] + [85\text{mg/kg x }0.075\text{kg}]}{0.025\text{ L} + [20\text{L/kg x }0.075\text{kg}]} = 4.18\text{ mg/L}$$

In this case, the maximum leachable concentration is below the 5 mg/1 regulatory concentration for lead, and the TCLP need not be performed.

Non-aqueous based wastes (i.e., oily wastes) may be calculated in the same manner as described above, except the concentration of constituents from the liquid portion of the waste (A in the above formula) are expressed in mg/kg units. Volumes also would be converted to weight units (kg). The final leachate concentration is expressed in mg/kg units.