4BLWP804.98 **AN UPDATE OF THE CURRENT STATUS OF THE RCRA METHODS DEVELOPMENT PROGRAM**

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Introduction

This article updates previous articles in *Environmental Lab* on the RCRA Methods Development Program focusing on the status of the SW-846 Updates and the progress that the Office of Solid Waste (OSW) has made in the RCRA Methods Development Program during the past two years. We will cover the advances that OSW has made in developing new methods as well as discussing the status of the SW-846 Updates. We will also report in depth on the progress in our major initiative to rewrite and update OSW's sampling guidance. We will also provide a clarification of OSW's policy on flexibility in using and modifying SW-846 methods and an update on the status of its implementation of the Performance-Based Measurement System (PBMS).

As in previous years, OSW's primary focus has been on improved sample preparation and cost-effective screening methods, as well as keeping SW-846 current with state-of-the-art developments in analytical instrumentation and methodology. We have also made significant progress in updating the sampling issues in SW-846, with regard to both sampling strategy and sampling methods.

Status of the Third Update

The Final Rule which incorporated Update III into the Third Edition of *Test Methods for Evaluating Solid Waste*, SW-846 was published in the *Federal Register* on Friday, June 13, 1997 (62 *FR* 32452). The FRN added 61 new methods and 37 revised methods to the Third Edition of SW-846 and deleted 16 obsolete methods from SW-846. We made no changes on method additions or deletions from those contained in the original Proposed Rule. Therefore, we will not take the time to repeat the list of the Update III methods in this article, since it has been covered extensively elsewhere. Update III is currently available both in hard copy (from the Government Printing Office) and in two electronic formats, a CD-Rom Version 2 of SW-846 with search capability (from the National Technical Information Service) and on the OSW Methods Team Home Page on the Internet at http://www.epa.gov/SW-846.

Status of the Fourth Update

OSW is putting out the Fourth Update to the Third Edition of *Test Methods for Evaluating Solid Waste* in two sections. The methods included in Update IVA, primarily

inorganic methods, were completed in the past two years. We wanted to get them out to the public in a timely manner and not hold up their distribution while waiting to complete the rest of the package. Update IVA was published as a Notice of Data Availability (NODA) in the *Federal Register* on May 8, 1998 (63 *FR* 25430). The comment period closed on June 22, 1998. The Update IVA NODA contains 12 new methods, 15 revised methods, one deleted method, and 43 flame and graphite furnace atomic absorption methods to be integrated into two generic AA methods (See Table 1). We will discuss these integrated methods in more detail in the Inorganic Methods Update section. Hard copies of the Update IVA methods can be obtained from GPO or NTIS. Electronic versions of the Update IVA methods can also be obtained from the OSW Methods Team Home Page on the Internet at http://www.epa.gov/epaoswer/hazwaste/test/up4a.htm.

OSW is currently working on a second part of Update IV, which includes primarily organic methods, to be published as another NODA. We expect to publish the Update IVB NODA in the *Federal Register* for public comment in the spring or early summer of 1999. The Update could possibly contain up to 50 methods, 20 new methods, 26 revised methods, and 4 air methods to be incorporated by reference (see Table 2). However, budget constraints and the need for additional development time may cause some of the methods tentatively scheduled for Update IVB (See Table 2) to be included in subsequent Updates. Draft Update IVB methods will be available from the Methods Team Office and from the Internet when they are completed. Announcements on the availability of these draft methods will be included in future issues of *Environmental Testing and Analysis.*

When and how the Update IV methods will be incorporated into SW-846, will depend on the progress of the Methods Reinvention Rule. This rule is intended to remove the unnecessary requirements to use SW-846 methods in the RCRA regulations and to allow OSW to issue Updates to SW-846 as guidance per the original intent of the document. We have included a more detailed discussion of this issue in the "PBMS Implementation" section of this article.

Method Flexibility and the Performance Based Measurement System (PBMS)

Historically, of all of EPA's regulatory program offices, OSW has allowed the most flexibility in methods selection and comes closest to implementing the PBMS for the RCRA Program. This allowance for methods flexibility and PBMS has been seriously misunderstood by both the regulators and the regulated community. We have attempted to clarify this allowable flexibility in Update III. We would like to briefly clarify OSW's policy on method flexibility and PBMS in this article. A more detailed discussion of these issues will be the topic of a future article.

Simply stated, OSW requires that the analyst must be able to demonstrate the ability to determine the analytes of concern in the matrix(ces) of concern at the [concentration] level of concern for any particular RCRA application, which we consider to be a PBMS approach. RCRA

regulations basically specify "what" needs to be determined and leaves the "how" up to the analyst. "Any reliable analytical method" (58 *FR* 46040) may be used for this demonstration. In a few instances under the RCRA regulations, which are listed in the promulgation of Update II (60 *FR* 3089), that "reliable analytical method" must be included in SW-846. For all other RCRA applications, SW-846 methods are not required to be used, but are provided as guidance to the analyst. Therefore, "OSW considers that SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods to be implemented by the user, as appropriate, in responding to RCRA-related sampling and analysis requirements."

Currently, the "Disclaimer" and "Preface and Overview" sections of SW-846 provide allowances for flexibility in methods selection and modification, and Section 2.1 of Chapter Two provides more specific guidance on how to implement this flexibility. The following language from the Preface and Overview should help clarify the intent of the SW-846 manual:

> "The procedures described in this manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it is possible to use this manual in rote fashion. In other situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes."

SW-846 methods are written so that they may be used as quantitative trace analytical methods to demonstrate that a waste "does not contain" constituents that require it to be managed as a hazardous waste. If particular RCRA applications do not require this rigor, looser analytical criteria may be applied, provided that they satisfy the data quality requirements for the particular application. Since data quality needs are project-specific in the RCRA Program, in order to successfully perform analyses it is necessary to address data quality issues prior to initiating any analyses. Good science dictates that, at a minimum, the following questions should be asked before beginning any analyses:

1) What is the purpose of this analysis? (Why are we doing this analysis?)

2) How (for what action) is the data generated from this analysis to be used?

3) What are the data quality needs for this project, i.e., how good does the data have to be to be useful for its intended purpose? (Including regulatory drivers, target analytes, matrices, concentration levels, statistical confidence levels, etc.)

The Agency once again emphasizes that the ultimate responsibility for producing reliable analytical results lies with the entity subject to the Federal, State, or local regulation. Thus,

members of the regulated community are advised to refer to the information in Chapter Two and to consult with knowledgeable laboratory personnel when choosing the most appropriate suite of analytical methods for any particular RCRA application. The regulated community is further advised that the methods in SW-846 or from other sources need only be used for those specific analytes of concern that are subject to regulation or other monitoring requirements.

Many of the determinative methods in SW-846 include performance data. These data are only intended as guidance on the performance that may be achieved in typical matrices and may be used by the analyst to select the appropriate method for the intended application. These performance data are not intended to be used as absolute QC acceptance criteria. Rather, each laboratory should develop actual performance criteria as described in Chapter Two and elsewhere in the manual for their particular applications. All methods used, either existing SW-846 methods, modified SW-846 methods, or methods from other sources should be documented in appropriate Sampling and Analysis Plans.

In summary, the methods included in SW-846 provide guidance to the analyst and the regulated community in making judgments necessary to generate data that meet the data quality needs or objectives for the intended use of the results.

PBMS Implementation for the RCRA Program

As we have mentioned previously, OSW has been operating in the PBMS mode for the most part, since its inception in the early 1980s. Because of the wide variety of the types of RCRA matrices, and many site-specific and project-specific applications, flexibility and the application of the PBMS approach in the use of analytical methods has been a necessity. As part of the overall Agency directive from the Agency's Deputy Administrator, Fred Hansen, to implement PBMS in all of its programs, OSW coordinated preparation of the PBMS Implementation Plan for the entire Office of Solid Waste and Emergency Response (OSWER). The OSWER plan was completed and submitted to the Deputy Administrator in April, 1998.

As stated in the OSWER PBMS Implementation Plan, OSW has initiated two major actions to remove some existing restrictions on method selection to improve method flexibility and to complete its move toward a more definitive PBMS approach to its regulatory policy. These two initiatives are 1) to remove the regulatory requirements for using SW-846 methods where they are not necessary, i.e, for analyses which do not require the use of method-defined parameters. By method-defined parameters, we mean methods that define a regulation and must be followed exactly to insure regulatory compliance, e.g., Method 1311-Toxicity Characteristic Leaching Procedure or Method 9095-Paint Filter Test for Free Liquid Determination); and 2) to include data quality requirements directly in RCRA regulations.

Currently, there are approximately 14 citations in the RCRA Subtitle C regulations which require the use of SW-846 methods for compliance. Several of these regulations require the use

of SW-846 methods for determining method-defined parameters, i.e., where the method is itself the regulation, (e.g., Method 9095-Paint Filter Test, Method 1311-TCLP, etc.). These are not subject to change nor are they applicable to a PBMS approach. However, the Agency is working to remove the unnecessarily rigid requirements in other regulations which currently require the use of SW-846 methods, e.g., filing delisting petitions and compliance with the Boiler, Incinerator and Furnace (BIF) Rules for parameter-defined methods. The completion of this "Methods Reinvention Rule" will allow the Agency to put out SW-846 methods as guidance, with the exception of the previously-mentioned method-defined parameters. In anticipation of the expected promulgation of this rule, OSW is issuing the Update IV methods as guidance. OSW expects to propose the Methods Reinvention Rule in the *Federal Register* by the end of this calendar year, with final promulgation expected by the end of December, 1999.

Secondly, in order to move towards a completely PBMS-based approach to regulations per Agency policy, OSW has begun to include data quality requirements directly in new RCRA regulations on a case-by-case basis. The first regulation promulgated under this PBMS approach is the Comparable Fuels Rule, which was published in the *Federal Register* in June, 1998. Others will follow. The direct incorporation of data quality requirements into the regulations should greatly assist both the regulators and the regulated community in facilitating methods selection for specific applications.

Training is of prime importance to the implementation of PBMS. OSW is heavily involved with the Agency's Environmental Monitoring Management Council (EMMC) in helping to develop Agency-wide PBMS training modules for a variety of target audiences. In addition, for the past four years, OSW has been actively providing program-specific training for EPA Headquarters and Regional and State personnel involved in RCRA regulatory activities that involve sampling and analysis. Two training modules have been developed. OSW presents the first module, "Analytical Strategy for the RCRA Program: A Performance-Based Approach", annually, in July, at the Waste Testing and Quality Assurance Symposium in Washington, DC and at a variety of other venues around the country. OSW also presents the second training module, "Basic RCRA Analytical Methods", a training module designed for non-chemists who must deal with analytical issues, at various venues around the country. OSW is working on training modules on sampling and the basics of chromatography, which we expect to complete some time in 1999.

Revisions to OSW's Sampling Guidance

The initial and perhaps most critical element in a program designed to evaluate the physical and chemical properties of a solid waste is the plan for sampling the waste. It is understandable that analytical studies, with their sophisticated instrumentation and high cost, are often perceived as the dominant element in a waste characterization program. Yet, despite that sophistication and high cost, analytical data generated by a scientifically defective sampling plan have limited utility, particularly in the case of regulatory proceedings. Chapters Nine and Ten of "Test Methods for

Evaluating Solid Waste, Physical/Chemical Methods", (SW-846), the RCRA test methods manual, address the development and implementation of a scientifically credible sampling plan for analyzing a solid waste. The principles to be considered in a performance-based sampling plan are delineated in these two chapters.

These chapters are being revised and expanded to account for this wide range of sample diversity that is encountered in the RCRA program. Chapter Nine is concerned with the big picture. It looks at the overall sampling plan including the data quality objective (DQO) process, the optimization of sampling design, and the data quality assessment (DQA) process. Chapter Ten is concerned with specific sampling strategies and techniques, for example, drums, waste piles, building debris, sampling tools, etc. These chapters were published in 1986 and have not been updated since despite the enormous increase in knowledge on the subject. The revision will include the latest information on the applied statistics necessary for designing a scientifically credible sampling plan for determining the hazard potential of wastes.

Sampling and analysis of waste material is not an end in itself, rather it is a component of a larger regulatory framework in which data collection, data quality and data interpretation are linked. This interrelationship is the key to the understanding and development of useful sampling guidance for the Office of Solid Waste. Environmental data collection for regulatory decision making and industry compliance must be of sufficient quality and quantity to support defensible decision making. This document will impart to our users a sound understanding of the data quality objective (DQO) process, modern sampling theory, applied statistics, and how existing and developing regulations drive the technical requirements of sampling and analysis guidance.

Consistent with the goals enumerated by OMB Circular A-119 and Public Law #104-113, the "Technology Transfer and Improvements Act of 1995", which requires Federal agencies to use consensus standards whenever possible, OSW is helping to support the American Society for Testing and Materials (ASTM) in developing improved sampling standards and methods for waste characterization, site assessment, and environmental monitoring. These standards along with current EPA sampling, analysis, and quality assurance documents form a nucleus from which OSW is developing updated sampling guidance for inclusion in Chapters Nine and Ten.

The philosophy regarding this revision of OSW's sampling guidance is as follows: SW-846 Chapters Nine and Ten must be user friendly, scientifically sound, statistically correct, legally enforceable, flexible, performance-based, and cost effective. EPA's guidance on readable regs and Vice President Gore's directive for the use of "plain language" in regulations and guidances is being implemented.

All commonly asked questions and reoccurring issues concerning OSW's current sampling guidance, especially those recorded on our MICE Line are being addressed in this revision.

The current status of the project is: draft #1 is complete and has been reviewed by sampling experts in ASTM Subcommittee D-34 Task Group. Based on ASTM's comments and review,

draft #2 should be complete by November 1998. EPA's Sampling Team, composed of representatives from OSW's Divisions, Regional RCRA Offices, and enforcement will begin reviewing draft #2 this winter. After EPA's internal review and revision, the final document should be ready for public distribution and comment by late spring of 1999.

Organic Methods Update

The primary focus of the RCRA Organic Methods Development Program over the past two years has continued to be on the use of innovative technologies for improving sample preparation methods and for developing cost-effective screening procedures. The Update IVA NODA contains 3 new methods, 10 revised methods and the deletion of the old manual headspace screening method, Method 3810 (See Table 1). As the Update IVB methods package gets closer to completion, it appears that it will most likely contain up to 17 new and 23 revised organic methods (See Table 2). In addition, 4 air methods from the Office of Air Quality, Planning and Standards (OAQPS) that may have use in the RCRA Program will also be incorporated by reference. Since many of these methods were covered in past articles, for the sake of brevity, we will only describe in limited detail new developments since that time.

We expect that the methods listed in Table 2 and described in both this section and the Inorganic Methods Update section of this article will be completed in time to be included in Update IVB. However, due either to budgetary constraints or unforeseen developmental difficulties, some of these methods may not be completed in time to make Update IV and will be included in subsequent Updates.

We will provide a brief review of the organic methods included in the Update IVA NODA. The sample preparation methods included are the new method, Method 3562-Organochlorine Pesticides and PCBs in Solid Matrices by SFE developed by the California Department of Food and Agriculture and Hewlett Packard and the expansion of the scope of the existing methods, Method 3535A-Solid Phase Extraction (SPE) by 3M Corporation and the Army's CRREL to include phenols, organophosphorus pesticides, phenoxyacid herbicides and explosives as additional analytes, and Method 3545A-Pressurized Fluid Extraction (PFE) by Dionex and the Ontario Ministry of Environment and Energy to include dioxins.

The other two new methods in the Update IVA NODA are the first quantitative immunoassay method included in SW-846, Method 4670-Triazines as Atrazine in Water by Immunoassay developed by Ohmicron and a Dexsil screening method for petroleum hydrocarbons in soil, Method 9074-Petroleum Hydrocarbons in Soil by Turbidimetric Analysis. The triazine method was developed for the Office of Water and they have notified us that Method 4670 will be incorporated into the Drinking Water regulations as an approved quantitative screening method.

The convention used in SW-846 organic methods dictates that performance data for analytical methods be included in the determinative method with a reference back to the sample

preparatory method used. The eight revised determinative methods in the Update IVA NODA (see Table 1) were revised based on the addition of performance data from the three sample preparative methods, Methods 3562, 3535A and 3545A.

Update IVA focused primarily on inorganic methods. Update IVB, however, focuses primarily on organic methods and will include several new technologies in the 17 potential new methods to be included.

Advances in immunoassay technology will be represented with two new types of immunoassay techniques. We expect that two immunosensor methods developed at the Naval Research Laboratory for TNT- and RDX-type explosives will be completed in time for inclusion in Update IVB. These methods, Method 4655-Explosives Analysis in Soil and Water Using Environmental Immunosensors and Method 4656:-Explosives Analysis in Soil and Water Using Fiber-Optic Immunosensors use immunoassay antibodies as sensors on a probe and different types of detectors. Another new type of immunoassay method, Method 4425-Screening Extracts of Environmental Samples for Planar Organic Compounds (PAHs, PCBs, Dioxins/ Furans) by a Reporter Gene on a Human Cell Line, developed by Columbia Analytical Services of Carlsbad, CA, utilizes a reporter gene to do a gross site screening for general compound classes of contaminants. There has also been some significant progress in the area of the original ELISA-type immunoassay methods. The development of Method 4025-Dioxin in Water and Soil by Immunoassay by Cape Technologies of South Portland, ME, is progressing well and validation is expected to be completed in time for its inclusion in Update IVB. In addition, the SW-846 Organic Methods Workgroup approved the validation studies submitted by Beacon Analytical Systems of Scarborough, ME for two new kits for inclusion in existing methods, one for PAHs (Method 4035) and the other for PCBs (Method 4020).

We expect to include these other screening methods in Update IVB. Method 8510-Field Method for the Determination of RDX in Soil, a test kit developed by CRREL and EnSys as a colorimetric analog to Method 8515 for TNT, finally completed its field and ruggedness testing at sites in Region 10 and was accepted by the Workgroup for inclusion in Update IVB. Method 8530-Field Method for Determination of THMs in Water, a colorimetric kit, also developed by EnSys, has completed field trials and has been accepted for inclusion in SW-846. Method 8540-Pentachlorophenol in Soil by UV-Induced Colorimetry developed by Envirol of Salt Lake City is a colorimetric method for screening pentachlorophenol in soils that was also accepted by the Workgroup. Method 8265-Volatiles by Direct Sampling Ion Trap Mass Spectrometry (IT-MS), developed by ORNL, has been field tested by the Army Corps of Engineers with a variety of direct sampling devices to introduce volatiles from air, water and soil matrices into the IT-MS for analysis. We are hoping to have this expanded version of Method 8265 completed in time for inclusion in Update IVB.

The Workgroup has accepted another important screening method for volatiles determination. With the development of new closed-system purge-and-trap (Method 5035) and headspace (Method 5021) sample preparation methods for soil samples containing either high and

low concentrations of VOAs, the question has often come up as to how to tell whether you need to use either a high concentration prep method or a low concentration prep method. Method 3815-Screening Procedure for Determination of Use of High or Low-Level VOA Procedures, developed by Alan Hewitt of CRREL, is designed to answer that question. It utilizes a portable photoionization detector (PID) to determine whether a high or low concentration of the principal site contaminants are present. Knowledge of the site contaminants is necessary to effectively use this technique and Method 3815 must *not* be used to decide that a sample or site is free of VOC contamination, or to decide that samples need not be collected for quantitative VOC analysis.

New sample preparation methods expected to be included in Update IVB are Method 3511-Microextraction Technique for Aqueous Matrices, Method 3570-Microextraction Technique for Soils and Solid Matrices, and Method 3546-Microwave Extraction. The two microextraction methods (Methods 3511 and 3570) were developed by the Electrical Power Research Institute (EPRI) and are intended to be used for the extraction of both volatile and semivolatile aromatic hydrocarbons, e.g., benzene, PAHs, in aqueous or solid matrices utilizing a rapid extraction technique with minimal solvent use. Method 3546 was developed by Environment Canada and is intended to be used as another rigorous rapid extraction technique analogous to PFE (Method 3545). Multilaboratory studies on analytes exhibiting the potential to undergo solvent-analyte interactions, i.e., phenols, organophosphorus pesticides, and phenoxyacid herbicides demonstrated that these analytes did not react under the extraction conditions of Method 3546.

Two new GC methods are expected to be included in Update IVB. These are Method 8085-Pesticides by GC/AED and Method 8095-Nitroaromatics and Nitramines by GC. Method 8085 is a method that was developed by the Washington Department of Ecology and Region X initially to screen pesticides using an atomic emission detector (AED) sensitive to the spectral lines emitted by the elements of interest. A multilaboratory validation study coordinated by Region X has confirmed that the method can also be used to quantitatively determine the analytes of concern. Method 8095 is a GC determinative method developed by CRREL for the explosive target analytes in Method 8330 and nitroglycerine. It utilizes an electron capture detector (ECD) and provides an alternative to HPLC for explosives analyses which can be used by laboratories that do not have or do not wish to use HPLC.

Two other new methods expected to be included in Update IVB for volatiles analysis are Method 8261-Volatile and Semivolatile Organic Compounds by Closed System Vacuum Distillation with Cryogenic Condensation and Mass Spectrometric Determination and Method 8450-Determination of Volatile Organic Compounds in Gaseous Samples by Fourier Transform Infrared (FT-IR) Spectroscopy. Method 8261 was developed by Mike Hiatt of NERL-LV and is based on a vacuum distillation and cryogenic trapping procedure (Method 5032) followed by gas chromatography/mass spectrometry. The method incorporates surrogate-based matrix correction, where the analysis of multiple samples is used to predict matrix effects by employing specific surrogates. As a result, the calculations involved are specific to Method 8261, and may not be used with data generated by another method. This method includes all the necessary steps from

sample preparation through instrumental analysis. Method 8450 was developed by the Idaho National Engineering Laboratory (INEL) for the headspace analysis of drums for VOAs by FTIR to determine whether or not they contained mixed waste.

The last new method that we expect to include in Update IVB is an air sampling method for acetonitrile from stacks, Method 0015-Acetonitrile from Stack Emissions by GC. The method is a stand-alone sampling and GC/FID analysis method for acetonitrile in stack gases. Since the method is stand-alone and is written exclusively for the determination of acetonitrile from stationary sources, we plan to place the method in Chapter 10 with the other air sampling procedures.

With regard to the revised methods to be included in Update IVB (See Table 2), the convention used in SW-846 organic methods dictates that performance data for analytical methods be included in the determinative method with a reference back to the sample preparatory method used. Most of the determinative methods in Table 2 are being revised because of the addition of new target analytes, as is also the case with the 3500 series extraction methods. We are revising the sample preparative methods for volatiles, (Methods 5021 and 5035) to include a reference to the high/low concentration screening method, (Method 3815). In addition, we are revising the volatile sample preparative and determinative methods for aqueous matrices (Methods 5030, 8021 and 8260) to reflect the inclusion of data from an ORNL holding time study that supports increasing the holding time for most volatile target analytes in preserved aqueous samples from 14 to 28 days. Exceptions to this new extended holding time will also be delineated.

Method 8310-Polynuclear Aromatic Hydrocarbons by HPLC is probably the oldest organic method in SW-846 not to have undergone revision. The Method 8310A version was initially planned to be revised to add the data from Method 3561-Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons. However, we now plan to update Method 8310A to bring it up-to-date with current technology, and include a completely revised version, written by Skip Weisberg of the Region III Laboratory in Annapolis into Update IVB. We are also revising another dated PAH method, Method 8100-Polynuclear Aromatic Hydrocarbons by Gas Chromatography. With data generously provided by Dennis Gere of Hewlett Packard and three graduate students from the University of Western Australia in Perth, we are bringing this method up to date as Method 8100A. We are also planning on increasing the guidance on how to run HPLC methods in Method 8000, the generic Chromatography method, as Method 8000C in Update IVB with contributions from Skip Weisberg and others.

As a final item regarding the organic methods in Update IVB, we are incorporating four OAQPS methods into SW-846 by reference (See Table 2). These methods either are referenced in current RCRA regulations or may be referenced in future RCRA regulations, so OSW has decided to include references to these methods in SW-846. We are not including the methods themselves, only references to where they can be found in their entirety in the EPA regulations.

Although development of new organic methodology was relatively slow for a few years for a variety of reasons, it has rapidly picked its pace over the past year. OSW expects to continue to prioritize its focus on new methods development activities. OSW solicits your input on new technologies for environmental monitoring that can improve upon existing SW-846 methods or expand the scope of the manual. We are particularly interested in those technologies which are faster, more cost effective, and create less waste than existing methods, yet with comparable precision and accuracy.

Inorganic Methods Update IVA

The focus of the RCRA Inorganic Methods Development Program over the past two years is the use of innovative technologies for improving sample preparation methods and for developing cost-effective screening procedures. Additionally, consolidation of analytical procedures has greatly streamlined the SW-846 inorganic methods.

The addition of new inorganic analytical technologies to SW-846 has progressed rapidly. Update IVA contains ten new methods and revises five existing methods and one chapter. Proven technologies introduced into Update IVA include: field-portable x-ray fluorescence spectrometry, capillary ion electrophoresis, ion-selective electrode potentiometry, immunoassay for metals, speciated isotope dilution, mercury by amalgamation/thermal desorption, atomic fluorescence spectroscopy, and improved microwave sample preparation.

Improved microwave sample preparation methods for aqueous and solid samples (Methods 3015A, Microwave Assisted Acid Digestion of Aqueous Samples and Extracts, and 3051A, Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils) are included in the Update IVA of SW-846. These methods, which allow for a mixed acid option, were developed jointly by OSW and by Dr. Skip Kingston, Dr. Peter J. Walter, and Dirk D. Link of Duquesne University. Use of mixed acids (hydrochloric and nitric) similar to the hot plate digestion procedures (Methods 3010A and 3050A) were studied for the microwave methods. Uniformity of results between hot plate and microwave methods and the addition of several new analytes to these methods was the major goal of these method improvements.

Field-portable XRF is a rapid, cost effective technique for environmental site assessment. The Office of Solid Waste(OSW) in collaboration with EPA's SITE Program demonstrated the power of this technology to rapidly characterize contaminated sites. The protocol for use of this technology is described in SW-846 Method 6200, Field-Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment, which is in Update IVA. This standardizes and promotes a technique which has received wide use in the environmental monitoring community.

Determination of Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis, Method 6500, offers an exciting new technology that is particularly adept at separating and

quantitating common inorganic anions. It is faster and less expensive than ion chromatography, but slightly less sensitive. Gary Fallick and Joe Romano of Waters and Roy-Keith Smith of ASI have been instrumental in helping us develop and validate this technology for this update. Hexavalent chromium analysis by capillary ion electrophoresis (Method 7194) has been studied by Don Miller of EPA Region 7. His procedure is under review for inclusion in a future SW-846 update.

Exciting new technologies are emerging from academia. Specifically, Dr. Skip Kingston and his graduate students at Duquesne University have developed isotope dilution as a reference method for speciating inorganic analytes. The technique has already proven effective for speciating between Cr^{+3} and Cr^{+6}. The great value of the method is as a standard reference protocol to help develop and validate other speciation procedures. Method 6800, Elemental and Speciated Isotope Dilution Mass Spectrometry, will have profound ramifications for the development of future speciation protocols.

The chemical and physical properties of mercury are unique among the elements. Method 7473, Analysis of Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry, exploits the unique chemistry of mercury to create a robust, highly specific and extremely sensitive technique for quantitative mercury analysis. Helen Boylan and Dr. Peter Walter of Duquesne University in Pittsburgh, PA developed and validated Method 7473 under the direction of Dr. Skip Kingston. Due to the severe toxicity of mercury and to its pervasive pre-RCRA mismanagement, EPA envisions widespread use of this technology especially in field applications.

The method has a dynamic range that spans approximately four orders of magnitude and the instrumental detection limit for this method is 0.01 ng total mercury. Method 7473 is designed for the determination of mercury in solids, aqueous samples, and digested solutions in both the laboratory and field environments. The stability of the instrument is such that field and lab results are statistically identical. Integration of thermal decomposition sample preparation, mercury separation by amalgamation and thermal desorption from a gold collector, and quantitation by atomic absorption spectrophotometry into one instrument reduces the total analysis time of most samples to less than five minutes in either the laboratory or field setting.

Method 7474, Determination of Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry, is another extremely sensitive technique for mercury analysis. OSW collaborated with Bill McDaniel and his staff at EPA's Region IV Laboratory in Athens, Georgia to propose this new technology in Update IVA. Atomic fluorescence has applicability to other important environmental analytes, specifically selenium and arsenic. We invite instrument vendors who have done development work on atomic fluorescence for Se and As to collaborate with us in order to help this technology grow in the environmental monitoring arena.

Mercury in Soil by Immunoassay, Method 4500, is in the Update IVA of SW-846, thanks to the efforts of Craig Schweitzer and Mal Riddell of BioNebraska. Data from several sites prove the reliability and cost-effectiveness of this fieldable screening technology. We expect to see other metal immunoassay kits developed in the future.

In the spirit of streamlining, all of the single element flame atomic absorption methods have been consolidated into Method 7000B, Flame Atomic Absorption Spectrophotometry. Method 7010, Graphite Furnace Atomic Absorption Spectrophotometry, was written to combine all the individual graphite furnace atomic absorption methods. This eliminates 42 AA and GFAA methods which are mostly boiler plate copies of each other, except for a few operational parameters which can easily be summarized in tables. During rulemaking for Updates II and III, several commenters suggested this consolidation and the Agency fully agrees. Also under study for future consolidation are the three aqueous digestion procedures (Methods 3005A, 3010A, and 3020A). These will be combined into Method 3000 if the data warrant.

Nitrite has be added to the list of ion-selective electrode potentiometric procedures (Method 9216, Potentiometric Determination of Nitrite in Aqueous Samples with Ion-Selective Electrode) based on method development and data from ATI Orion. The procedure quantitatively measures the concentration of nitrite in aqueous solutions.

A method for determining the percentage of water in waste is often needed for mass balance studies, for the aqueous alcohol solution exclusion in the ignitability regulations, and for determining if a liquid is aqueous or non-aqueous for pH measurement under the corrosivity characteristic. This is provided in Method 9000, Determination of Water in Waste Materials by Karl Fischer Titration. OSW collaborated with EPA's National Enforcement Investigation Center (NEIC) in Denver, Colorado and Alvia Gaskill of Environmental Reference Materials, in the development of this method. Method 9001, Determination of Water in Waste Materials by Quantitative Calcium Hydride Reaction, was also developed by Mr. Gaskill. It is an elegant, accurate, and simple technology that measures free water by the gas generated from the reaction of the water with calcium hydride.

Two additional methods were revised for Update IVA. Method 6020A, Inductively Coupled Plasma - Mass Spectrometry, was updated to add additional analytes. Method 7471B, Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique) was revised to clarify the great triplicate digestion controversy. The ambiguous wording in Method 7471A has caused us and laboratories numerous difficulties. We have revised Method 7471A in order to clarify the language.

From discussions we have had with many scientists at EPA, it appears that the intent of triplicate weighings is to obtain a representative sample (i.e. 3 portions taken from different places in the sample container). This is a sampling problem not an instrumental analysis problem. The major variance is caused by laboratory subsampling not by the analytical determination. The revision of the method stresses the need to thoroughly mix/homogenize the sample before weighing out the

analytical aliquot. We have modified Method 7471A to require the digestion of a single 0.5 to 0.6 g sample. Requiring a larger sample offers the following advantages over the current 0.2 g approach: lower detection limit, analysis less dependent on sample homogeneity, more consistent treatment of Hg with respect to other metals under SW-846, more consistent with other prep methods for Hg (Method 3051 requires 0.5g), and data handling , reporting and validation concerns due to "triplicate analysis" interpretation are eliminated. Performing the analysis in triplicate dramatically increases costs to the environmental community and does not significantly add to the quality of the data generated. The environment would be better served by analyzing more samples, rather than by doing repeated analyses of the same sample.

SW-846 Chapter 3 was revised to add additional information on sample preparation considerations and on clean laboratory procedures.

Inorganic Methods Update IVB

Update IVB scheduled for the spring of 1999, adds three new methods, revises three existing methods, and revises definitions in SW-846 Chapter 3**.** Two of the new methods, give testing procedures which are useful guidance but not required methods for the characteristics. They are: Method 1040, Test Method for Oxidizing Solids, and Method 1050, Test Method to Determine Substances Liable to Spontaneous Combustion. Both are adopted from the Department of Transportation regulations and the United Nations “Recommendations on the Transportation of Dangerous Goods.”

The third new procedure, Method 9058, Determination of Perchlorate by Ion Chromatography, adds a new analyte to the IC technology which is becoming important to monitor at selected sites.

Method 6010C, Inductively Coupled Plasma-Atomic Emission Spectroscopy, is being revised to incorporate improved quality assurance criteria which is in conformance with the Update IVA revisions to the AA and GFAA methods. Joe Solsky with the U.S. Army Corp of Engineers has provided extensive expert help and guidance to OSW in this work. The Corps hands on experience with all our major methods, give them a unique perspective for improving the quality and clarity of SW-846 procedures for all required users of RCRA methods.

Method 9056A, Determination of Inorganic Anions by Ion Chromatography, is being revised to correct some inconsistences in QA guidance and to incorporate improvements in IC technology that have occurred over the six years since its initial proposal.

Method 9210A, Potentiometric Determination of Nitrate in Aqueous Samples with Ion-Selective Electrode, is being revised to correct a problem with calibration standards.

Future Directions

General directions for the RCRA program include: continued development of cost effective screening methods, continued improvement of sample preparation methods, with particular emphasis on reduction of the use of hazardous substances, and continued development of cost effective analytical methods that can be used directly on site.

Specific directions for the RCRA methods development program are being charted by government regulatory needs, analytical technology development, and basic research coming from academia. New technologies that address our needs and that are well validated for the analytes and matrices of interest will find enthusiastic acceptance into OSW's method development program.

Some specific organic projects include continued development of Fourier Transform Infrared (FTIR) methods for headspace determination of volatile organics, continued development of new types of immunoassay products including quantitative techniques, affinity chromatography, development of new HPLC methods, and evaluation of capillary zone electrophoresis (CZE) for RCRA organic target analytes.

Future inorganic methods for SW-846 may incorporate the following emerging technologies and applied research: laser ablation spectrophotometry, immunoassay for other inorganic analytes, new reactive cyanide and sulfide procedures, new procedures for speciating the various complex forms of cyanide, field-portable potentiometric stripping analyzers, and speciation of mercury by determination of organic, inorganic, and elemental forms of mercury in soils and waste. OSW solicits your input on new technologies for environmental monitoring that can improve upon existing SW-846 methods or expand the scope of the manual. We are particularly interested in those technologies which are faster, more cost effective, and create less waste than existing methods, yet with comparable precision and accuracy.

TABLE 1: UPDATE IVA

NEW METHODS[a]

Method 3562: Organochlorine Pesticides and PCBs in Solid Matrices by SFE

Method 4500: Mercury in Soil by Immunoassay

Method 4670: Triazines as Atrazine in Water by Immunoassay

Method 6200: Field-Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment

Method 6500: Determination of Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis

Method 6800: Elemental and Speciated Isotope Dilution Mass Spectrometry (Duquesne University)

Method 7010: Graphite Furnace Atomic Absorption Spectrophotometry (Consolidate all GFAA methods)

Method 7473; Analysis of Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry (Duquesne University)

Method 7474: Determination of Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry

Method 9000: Determination of Water in Waste Materials by Karl Fischer Titration

Method 9001: Determination of Water in Waste Materials by Quantitative Calcium Hydride Reaction (Alvia Gaskill & Dexsil Corp.)

Method 9074: Petroleum Hydrocarbons in Soil by Turbidimetric Analysis

Method 9216: Potentiometric Determination of Nitrite in Aqueous Samples with Ion-Selective Electrode

[a] Absence of a suffix following the Method No. indicates Revision 0

REVISED METHODS[b]

Method 3015A: Microwave Assisted Acid Digestion of Aqueous Samples and Extracts

Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils

Method 3535A: Solid Phase Extraction Disk Method (SPE)

Method 3545A: Pressurized Fluid Extraction (PFE)

Method 6020A: Inductively Coupled Plasma - Mass Spectrometry

Method 7000B: Flame Atomic Absorption Spectrophotometry

Method 7471B: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)

Method 8081B: Organochlorine Pesticides by Gas Chromatography: Capillary Column Technique

Method 8082A: Polychlorinated Biphenyls (PCBs) by Gas Chromatography: Capillary Column Technique

Method 8141B: Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique

Method 8270D: Semivolatile Organic Compounds by GC/MS: Capillary Technique

Method 8280B: Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans

Method 8290A: Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)

Method 8321B: Solvent-Extractable Non-volatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry or Ultraviolet (UV) Detection

Method 8330A: Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)

[b] Suffixes following the Method No. indicate that a method has been revised and reissued:

A indicates Revision 1
B indicates Revision 2
C indicates Revision 3, etc.

DELETED AND INTEGRATED METHODS[b]

Method 3810[c]: Headspace

Method 7020[d]: Aluminum (AA, Direct Aspiration)

Method 7040[d]: Antimony (AA, Direct Aspiration)

Method 7041[e]: Antimony (AA, Furnace Technique)

Method 7060A[e]: Arsenic (AA, Furnace Technique)

Method 7080A[d]: Barium (AA, Direct Aspiration)

Method 7081[e]: Barium (AA, Furnace Technique)

Method 7090[d]: Beryllium (AA, Direct Aspiration)

Method 7091[e]: Beryllium (AA, Furnace Technique)

Method 7130[d]: Cadmium (AA, Direct Aspiration)

Method 7131A[e]: Cadmium (AA, Furnace Technique)

Method 7140[d]: Calcium (AA, Direct Aspiration)

Method 7190[d]: Chromium (AA, Direct Aspiration)

Method 7191[e]: Chromium (AA, Furnace Technique)

Method 7200[d]: Cobalt (AA, Direct Aspiration)

Method 7201[e]: Cobalt (AA, Furnace Technique)

Method 7210[d]: Copper (AA, Direct Aspiration)

Method 7211[e]: Copper (AA, Furnace Technique)

Method 7380[d]: Iron (AA, Direct Aspiration)

Method 7381[e]: Iron (AA, Furnace Technique)

Method 7420[d]: Lead (AA, Direct Aspiration)

Method 7421[e]: Lead (AA, Furnace Technique)

Method 7430[d]: Lithium (AA, Direct Aspiration)

Method 7450[d]: Magnesium (AA, Direct Aspiration)

Method 7460[d]: Manganese (AA, Direct Aspiration)

Method 7461[e]: Manganese (AA, Furnace Technique)

Method 7480[d]: Molybdenum (AA, Direct Aspiration)

Method 7481[e]: Molybdenum (AA, Furnace Technique)

Method 7520[d]: Nickel (AA, Direct Aspiration)

Method 7521[e]: Nickel (Atomic Absorption, Furnace Method)

Method 7550[d]: Osmium (AA, Direct Aspiration)

Method 7610[d]: Potassium (AA, Direct Aspiration)

Method 7740[e]: Selenium (AA, Furnace Technique)

Method 7760A[d]: Silver (AA, Direct Aspiration)

Method 7761[e]: Silver (AA, Furnace Technique)

Method 7770[d]: Sodium (AA, Direct Aspiration)

Method 7780[d]: Strontium (AA, Direct Aspiration)

Method 7840[d]: Thallium (AA, Direct Aspiration)

Method 7841[e]: Thallium (AA, Furnace Technique)

Method 7870[d]: Tin (AA, Direct Aspiration)

Method 7910[d]: Vanadium (AA, Direct Aspiration)

Method 7911[e]: Vanadium (AA, Furnace Technique)

Method 7950[d]: Zinc (AA, Direct Aspiration)

Method 7951[e]: Zinc (AA, Furnace Technique)

[b] Suffixes following the Method No. indicate that a method has been revised and reissued:

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[c] Method to be deleted (Replaced by Method 5021)

[d] Flame AA method to be integrated into Method 7000B

[e] Furnace AA method to be integrated into Method 7010

TABLE 2: UPDATE IVB

NEW METHODS[a]

Method 0015:	Acetonitrile from Stack Emissions by GC
Method 1040:	Test Method for Oxidizing Solids
Method 1050:	Test Method to Determine Substances Liable to Spontaneous Combustion
Method 3511:	Microextraction Technique for Aqueous Matrices
Method 3546:	Microwave Extraction
Method 3570:	Microextraction Technique for Soils and Solid Matrices
Method 3815:	Screening Procedure for Determination of Use of High or Low-Level VOA Procedures
Method 4025:	Dioxin in Water and Soil by Immunoassay
Method 4425:	Screening Extracts of Environmental Samples for Planar Organic Compounds (PAHs, PCBs, Dioxins/ Furans) by a Reporter Gene on a Human Cell Line
Method 4655:	Explosives Analysis in Soil and Water Using Environmental Immunosensors
Method 4656:	Explosives Analysis in Soil and Water Using Fiber-Optic Immunosensors
Method 8085:	Pesticides by GC/AED
Method 8095:	Nitroaromatics and Nitramines by GC (CRREL)
Method 8261:	Volatile and Semivolatile Organic Compounds by Closed System Vacuum Distillation with Cryogenic Condensation and Mass Spectrometric Determination
Method 8265:	Volatiles in Water by Direct Sampling Ion Trap Mass Spectrometry (ORNL)
Method 8450:	Determination of Volatile Organic Compounds in Gaseous Samples by Fourier Transform Infrared (FT-IR) Spectroscopy (INEL)

Method 8510: Field Method for the Determination of RDX in Soil

Method 8530: Field Method for Determination of THMs in Water

Method 8540: Pentachlorophenol (PCP) in Soil and Water by UV-Induced Colorimetry

Method 9058: Determination of Perchlorate by Ion Chromatography

[a] Absence of a suffix following the Method No. indicates Revision 0

REVISED METHODS[b]

Method 3500C: Organic Extraction and Sample Preparation

Method 3535A: Solid Phase Extraction Disk Method (SPE) (Rev 1A),

Method 3545A: Pressurized Fluid Extraction (PFE) (Rev. 1A)

Method 3550C: Ultrasonic Extraction

Method 3620C: Florisil Cleanup

Method 5000A: Sample Preparation for Volatile Organic Compounds

Method 5021A: Volatile Organic Compounds in Solid Matrices Using Automated Static Headspace Apparatus

Method 5030C: Volatile Organic Compounds in Aqueous Matrices by the Purge and Trap Procedure

Method 5032A: Volatile Organic Compounds by Vacuum Distillation

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

Method 6010C: Inductively Coupled Plasma-Atomic Emission Spectroscopy

Method 8000C: Chromatography

Method 8021C: Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors

Method 8041A: Phenols by Gas Chromatography

Method 8082B: Polychlorinated Biphenyls (PCBs) by Gas Chromatography

Method 8100A: Polynuclear Aromatic Hydrocarbons by Gas Chromatography

Method 8141B: Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique (Rev. 2A)

Method 8151B: Chlorinated Herbicides by Gas Chromatography: Capillary Column Technique

Method 8260C: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

Method 8270D: Semivolatile Organic Compounds by GC/MS: Capillary Technique (Rev. 4A),

Method 8290A: Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) (Rev. 1A)

Method 8310A: Polynuclear Aromatic Hydrocarbons by HPLC

Method 8318A: N-Methyl Carbamates by High Performance Liquid Chromatography (HPLC)

Method 8321B: Solvent-Extractable Non-volatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry or Ultraviolet (UV) Detection (Rev 2A)

Method 9056A: Determination of Inorganic Anions by Ion Chromatography

Method 9210A: Potentiometric Determination of Nitrate in Aqueous Samples with Ion-Selective Electrode

[b] Suffixes following the Method No. indicate that a method has been revised and reissued:

A indicates Revision 1
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METHODS INCORPORATED BY REFERENCE

Method 25D: Determination of the Volatile Organic Content of Waste Samples (40 CFR 60, Appendix A)

Method 25E: Determination of Vapor Phase Organic Concentration in Waste Samples (40 CFR 60, Appendix A)

Method 207-1: Sampling Method for Isocyanates

Method 207-2: Analysis for Isocyanates by High Performance Liquid Chromatography (HPLC)