AN UPDATE OF THE CURRENT STATUS OF THE RCRA METHODS DEVELOPMENT PROGRAM

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Introduction

This article updates our previous articles in *Environmental Testing & Analysis* and will cover the activities of the OSW Methods Team in advancing the RCRA Methods Development Program over the past twelve months. We will discuss the new methods that we have either pursued or received since last year, and update some sections of last year's overview, as well as the status of the SW-846 Updates. We will continue to provide a clarification of OSW's policy on flexibility in using and modifying SW-846 methods, and new developments 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. This past year, we have made significant progress in upgrading the quality of the Methods Team Homepage to provide useful and timely electronic information on the SW-846 Methods Program (www.epa.gov/SW-846).

Status of the Fourth Update

Update IVB

Through an administrative action, OSW was directed to publish a *Federal Register* Notice for Update IVB for public comment as another Notice of Data Availability (NODA). Due to time constraints for its publication, the Update IVB NODA will contain the 31 methods that were completed by September 30, 2000 (See Table 1 for a list of the Update IVB methods). The Update IVB package contains 12 new methods, 15 revised methods, and 4 air methods that are being incorporated by reference. All of these methods can be found on the Methods Team Homepage at www.epa.gov/SW-846.

When and how the Update IV methods will be incorporated into SW-846, will depend on the progress of the Methods Reinvention Rule, which is nearing the proposal stage. 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 continued our attempts to clarify this allowable flexibility in Update III, and in a series of articles, presentations and training courses presented this past year. We believe that we covered the major issues in reasonable detail in the last article, and see no need to repeat them here. However, in a recent article in *LC-GC* magazine (Reference 1), we have covered the issue of method user validation or "demonstration of

applicability" in great detail, and show how it differs from validation of a new method by the developer. In addition, in a future issue of *ET&A*, we will discuss in detail how to use PBMS effectively in the systematic planning process for projects. The article is based on a real world example of an OSW study of non-RCRA regulated surface impoundments.

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 we stated in our last *ET&A* article, OSW has continued implementing its two major activities 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 actions are 1) "Methods Reinvention Rule" 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; and 2) to include data quality requirements directly in RCRA regulations. By method-defined parameters, we mean methods that define a regulation and must be followed exactly to insure regulatory compliance, such as Method 1311-Toxicity Characteristic Leaching Procedure or Method 9095-Paint Filter Test for Free Liquid Determination).

Work is continuing on the proposal of the Methods Reinvention Rule. 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* some time in 2001, with promulgation of the Final Rule expected in 2002.

In order to move towards a completely PBMS-based approach to regulations per Agency policy, OSW has continued to include data quality requirements directly in new RCRA regulations on a case-by-case basis. The first regulation promulgated under this PBMS approach was the Comparable Fuels Rule, which was published in the *Federal Register* in June, 1998. Others have followed including promulgation of the combustion or Maximum Achievable Control Technology (MACT) Rule and proposal of the Chlorinated Solvents and Dyes and Pigments Listings in 1999 and its promulgation in 2000. Other concentration-based listing rules in process also include data quality requirement language. 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 continues to be heavily involved with the Agency's PBMS Training Workgroup in developing Agency-wide PBMS training modules for a variety of target audiences. In addition, for the past six years, OSW has actively provided program-specific training for EPA Headquarters, EPA Regional, and State personnel involved in RCRA regulatory activities that involve sampling and analysis, as well as the general public. We have developed two training PBMS modules, one dealing with analytical strategy for preparing sampling and analysis plans (SAPs) using the PBMS approach and the other dealing with PBMS in regulations. OSW presents these modules, "Analytical Strategy for the RCRA Program: A Performance-Based Approach" and "What is PBMS?", annually, in July, at the Waste Testing and Quality Assurance Symposium (WTQA) in Washington, DC and at a variety of other sites around the country. OSW also presents another training module, "Basic RCRA Analytical Methods", designed for non-chemists who must deal with analytical issues, at various sites around the country. OSW is working on training modules on sampling and has completed a training course on the basics of chromatography in collaboration with partners from the U.S. Army Corps of Engineers and industry. The Basic Chromatography course was first presented at the

1999 WTQA Symposium.

Electronic Documents and Information

In last year's *ET&A* article, we described in detail the Internet and CD-ROM services that the Methods Team offers to the environmental analytical community. The only item that we will discuss here is our recent upgrade of the Methods Team Homepage.

The OSW Methods Team put out its new improved Homepage on the EPA Website on Friday, August 4, 2000. The revised Homepage makes searching easier by placing all of the subject headings as buttons in the left-hand column. However, the most significant improvement over the previous version is the ability to access the Update IVA and IVB methods directly from the SW-846 Manual heading, rather than the roundabout way it had to be done before. The new Homepage is also fully compliant with the Federal requirements for access by persons with disabilities. The Homepage address remains the same at www.epa.gov/SW-846 and should still work with any previously-existing bookmarks for the site.

MICE Service

The Methods Team is continuing to support its highly successful technical information service on RCRA-related analytical issues, the Methods Information Communication Exchange (MICE). The MICE service can be reached either by telephone at 703-676-4690 or by e-mail at mice@cpmx.saic.com for leaving method-related questions and comments on technical issues regarding SW-846. Responses are usually handled within one working day.

Organic Methods Update

The primary focus of the RCRA Organic Methods Development Program over the past several years has continued to be on the use of innovative technologies for improving sample preparation methods and for developing cost-effective screening procedures. An additional area of focus for us is updating methods using obsolete equipment. In this section, we will only cover additional developments to methods discussed in the last article and the new additions.

The 31 methods completed for inclusion in the Update IVB NODA are listed in Table 1. Of the 25 organic methods included, all but the two new screening methods for RDX in soil (Method 8510) and for pentachlorophenol in soil (Method 8540) were covered in previous overview articles. Method 8510 is the RDX analog to Method 8515 for TNT and is covered in detail in the July/August, 2000 issue of *ET&A*. Method 8540 is a screening method for PCP in soil at contaminated sites that uses extraction and derivatization steps leading to a UV determination.

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 over the course of the next year as draft SW-846 methods. Most are far enough along in their development and validation to be completed this year. However, due either to budgetary constraints, unforeseen developmental difficulties or changes in priorities, some of these methods may not be completed as planned. These methods will be posted on the Methods Team Homepage as they are completed.

Here is an update on the status of the immunoassay methods discussed in the last article. Some difficulties encountered in the validations of the two immunosensor methods developed at the Naval Research Laboratory for TNT- and RDX-type explosives have been resolved and we expect to move forward with completion of draft Methods 4655 (Flow Cell Detection) and 4656 (Fiberoptic Detection). Method 4025-Dioxin in Water and Soil by Immunoassay, developed by

Cape Technologies, is in the final stages of validation and we expect the validation report for Workgroup review in the near future. Method 4026, also developed by Cape Technologies for the analysis of coplanar PCBs will be the subject of a field validation project later this year.

Oak Ridge National Laboratory (ORNL) has resumed work on the expansion of scope of the Direct Sampling Ion Trap Mass Spectrometry method for VOAs in water and other media (Method 8265). The method is in its final edit stage and should appear on the Methods Team website in the next few months.

Two ongoing method development projects between OSW and industry are the adaptation of electrospray HPLC/MS (tentatively Method 8322) to replace the obsolete Thermospray interface in Method 8321 and the development of a capillary electrophoresis method for polar organic analytes (Method 8355). Both are currently in the optimization of procedure stage. If anyone is interested in participating in the multilaboratory validations of either of these two methods early next year please let us know by e-mail at lesnik.barry@epa.gov.

Because of the significant quantity of data that has been generated over the last couple of years using a variety of viable sample handling techniques for VOAs in soils, we have made the generation of a guidance document on appropriate ways to prepare VOA samples and revision of the appropriate VOA sample preparative and determinative methods a priority for the next year. We are in process of preparing a draft of this guidance document which we will put up on the Methods Team website for comment.

Two other methods that we plan to update to incorporate more modern equipment and chromatographic techniques are Method 8290A-Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) and Method 8310A-Polynuclear Aromatic Hydrocarbons by HPLC. If time allows, we would also like to include an update of Method 8100-PAHs by GC as well. All of these methods were developed in the 1980s and need to be modernized to reflect how they should be performed with modern equipment.

Although development of new organic methodology was relatively slow for a few years for a variety of reasons, it has rapidly picked up its pace over the past two years. 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. If you are interested in working with us on a new organic methods project, please contact us at the above e-mail address.

Inorganic Methods Update

The focus of the RCRA Inorganic Methods Development Program over the past year has been on the development of screening procedures, and on the speciation of highly toxic inorganic analytes. We expect that the speciation projects begun last year will result in viable methods in the next several months.

Mercury continues to be a “hot” topic for OSW.. Because of the widely varying toxicities of different chemical species of mercury, a method is needed to distinguish between mercury’s different chemical forms. Method 3200-Determination of Mercury Species in Soil by Selective Solvent Extraction and Acid Digestion, is a separation and analysis scheme for the speciation of mercury (organic, inorganic, and elemental) that fills this void. Preliminary work was done in this area by EPA’s Office of Research and Development. Their work is being greatly expanded,

validated, and drafted into a standard laboratory method by Dr. Skip Kingston and his students at Duquesne University. Continuation of this mercury speciation project will involve testing for biological tissues (tuna fish, dogfish muscle), and botanical matrices (mushroom). Method 3200 will also be validated using different SRMs and CRMs for soil, sediments, biological tissues, and botanical matrices. High performance liquid chromatography (HPLC) will be coupled with the most sensitive elemental detection method inductively coupled plasma mass spectrometry (ICP-MS) to perform mercury speciation studies. Method 7473, a rapid technique for the determination of total mercury in environmental and biological samples, will be used to compare results obtained from HPLC-ICP-MS.

In another aspect of this study, because some inorganic mercury may transform into methylmercury, or vis-versa during extraction or digestion process, Method 6800-Elemental and Speciated Isotope Dilution Mass Spectrometry, will be used as a diagnostic and validation tool for these selective extraction studies. Method 6800 is a definitive technique that overcomes many problems associated with instrumental drift and incomplete extraction of analytes from sample matrices. Method 6800 uses isotopically labeled species to monitor species transformations occurring during sample preparation and analysis procedures. By measuring the altered isotope ratio of the species of interest, the intertransformation of these species can be resolved mathematically. Other major advantages include the exceptional precision and accuracy offered by this method. Transformations that occur in specific samples will be evaluated to suggest corrective action for Method 3200 and possible alterations to improve the more traditional 3200 method. Method 6800 will be demonstrated for methylmercury. Specific interferences in method 3200 and specific samples and species of mercury will be evaluated.

Method 6300-Identification of Crystalline Materials by X-ray Powder Diffraction, is a technology long overdue for inclusion in EPA's arsenal of environmental monitoring methods. X-ray Diffraction (XRD) is a well known, highly developed technology for the identification of crystalline materials. It has been used for many years in industry and by the geological community. It has many unique features that make it an attractive technology for environmental monitoring. Knowing the exact molecular form of a waste is often more important than knowing the concentration of each individual element. For example, proving chromium is present in a waste as chromite ($FeCr_2O_4$) where the chromium is insoluble, trivalent, and is not bioavailable rather than as chromium trioxide (CrO_3) where the chromium is soluble, hexavalent, bioavailable, highly toxic, and the compound is corrosive and a powerful oxidizing agent, is an extremely important piece of information in determining the management of the waste. David Frank of EPA Region 10, Doug Kendall of NEIC, and Dave Bartenfelder of OSW have expertise in XRD and are working with us on the development of this method along with input from instrument vendors. The draft Method 6300 has gone through Workgroup review, and is nearing completion and we expect it to be added to the Methods Team website in the next few months.

When dealing with unknown solid materials, the number one question is "What is it?". In environmental analysis of solids, no other technology currently exists that can answer this question as rapidly, completely, or unambiguously as X-ray diffraction especially coupled with quantitative chemical information. Unknown solids are a common occurrence at Superfund sites. Thus, the CERCLA program should find widespread application and benefit from this technology. Knowing the composition of solid phases present at a site or in a waste will help us (1) trace its source, (2) identify its routes of transport, (3) determine its fate, and (4) guide us in the best methods of treatment or removal. This method will fill a monitoring niche for which there are currently no applicable methods published in the environmental area. The technology is well developed for geological applications and industrial quality control and analysis. XRD is a prime candidate to adapt for environmental analytical applications.

Another major project for the coming year is the expansion of the immunoassay methods program for metals. Method 4500 for mercury was included in Update IVA. We are currently

working with Dr. David Johnson of BioMetallix, Inc., on another immunoassay method, Method 4510-Lead in Water and Soil by Fluorescence Polarization Immunoassay. The preliminary tests have been very encouraging and we are planning on doing significant field studies to validate the method over the next several months.

Two other methods that went through Workgroup review this summer and are in the final stages of review and validation are Method 9015-Metal Cyanide Complexes by Anion Exchange Chromatography and UV Detection and Method 6250-X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Environmental Samples. Method 9015 was developed by Sharon Drop of ALCOA and covers the determination of metal cyanide complexes of iron, cobalt, silver, gold, copper, and nickel in water, wastewater, leachate, and solid wastes using anion exchange chromatography and UV detection. Method 6250 was developed in collaboration with instrument manufacturers and Doug Kendall of EPA's NEIC laboratory. It describes the use of both energy dispersive X-ray fluorescence (EDXRF) spectrometers and wavelength dispersive X-ray fluorescence (WDXRF) spectrometers for the quantitative determination of elemental concentrations in environmental matrices. Use of X-ray fluorescence (XRF) allows for rapid multi-element analysis, often with minimal sample preparation. Generally elements of atomic number 16 or greater can be detected and quantitated by XRF.

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 (i.e., the so-called "green methods"), 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, immunosensors and affinity chromatography, development of new HPLC methods, and evaluation of capillary zone electrophoresis (CZE) for RCRA organic target analytes. We are also working on evaluating an in situ TCE sensor developed by Burge Environmental at an Air Force site, the results of which will be presented in a future article.

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 chemical reactivity with water (evolution of ignitable or toxic gases).

OSW actively 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.

References

1. B. Lesnik, "Method Validation Issues for the RCRA Program", *LC-GC*, October, 2000

TABLE 1: METHODS INCLUDED IN UPDATE IVB

4TH UPDATE (PART 2)-NEW METHODS[a]

Method 1040:	Test Method for Oxidizing Solids
Method 1050:	Test Method to Determine Substances Liable to Spontaneous Combustion
Method 3546:	Microwave Extraction
Method 3815:	Screening Procedure for Determination of Use of High or Low-Level VOA Procedures
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 8085:	Pesticides by GC/AES
Method 8095:	Nitroaromatics and Nitramines by GC
Method 8261:	Volatile and Semivolatile Organic Compounds by Closed System Vacuum Distillation with Cryogenic Condensation and Mass Spectrometric Determination
Method 8510:	Field Method for the Determination of RDX in Soil
Method 8535:	Quick Method for Determination of TCE and Other Halogenated Aliphatic Hydrocarbons in Water
Method 8540:	Pentachlorophenol (PCP) by UV-Induced Colorimetry
Method 9058:	Determination of Perchlorate by Ion Chromatography

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

4TH UPDATE (PART 2)-REVISED METHODS[b]

Method 3500C:	Organic Extraction and Sample Preparation
Method 3535A:	Solid Phase Extraction Disk Method (SPE)
Method 3545A:	Pressurized Fluid Extraction (PFE)
Method 3550C:	Ultrasonic Extraction
Method 3620C:	Florisil Cleanup
Method 6010C:	Inductively Coupled Plasma-Atomic Emission Spectroscopy
Method 8015C:	Nonhalogenated Volatile Organics by GC/FID
Method 8041A:	Phenols by Gas Chromatography

Method 8081B: Organochlorine Pesticides by Gas Chromatography

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

Method 8141B: Organophosphorus Compounds by Gas Chromatography

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

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
B indicates Revision 2
C indicates Revision 3, etc.

4TH UPDATE (PART 2)-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)

TABLE 2: METHODS IN PROCESS

New Methods

Method 3200:	Determination of Organic, Inorganic, and Total Mercury in Soils
Method 4025:	Dioxin in Water and Soil by Immunoassay
Method 4026:	Coplanar PCBs in Water and Soil by Immunoassay
Method 4430:	Dioxin TEQ by DELFIA Immunoassay
Method 4510:	Lead in Water and Soil by Immunoassay
Method 4655:	Explosives Analysis in Soil and Water Using Environmental Immunosensors
Method 4656:	Explosives Analysis in Soil and Water Using Fiber-Optic Immunosensors
Method 6250:	X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Environmental Samples
Method 6300:	X-ray Diffraction for the Determination of Crystalline Phases in Environmental Samples
Method 8265:	Volatiles in Water by Direct Sampling Ion Trap Mass Spectrometry (ORNL)
Method 8322:	Solvent-Extractable Non-volatile Compounds by High Performance Liquid Chromatography/Electrospray/Mass Spectrometry or Ultraviolet (UV) Detection
Method 8355:	Polar Organic Compounds by Capillary Electrophoresis
Method 9015:	Total Dissolved Iron Cyanide by Ion Chromatography

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

Revised Methods

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 8000C: Chromatography

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

Method 8151B: Chlorinated Herbicides by Gas Chromatography

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

Method 8270E: Semivolatile Organic Compounds by GC/MS

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

Method 8310A: Polynuclear Aromatic Hydrocarbons by 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.

METHODS INCORPORATED BY REFERENCE

Method 0100A: Sampling for Formaldehyde and Other Carbonyl Compounds in Ambient Air (replace with current version from [Compendium of Methods for the Determination of Toxic Organic Chemicals in Ambient Air. Report No. EPA/600/R-96/010b. Cincinnati, OH: U.S. Environmental Protection Agency, Office of Research and Development http://www.epa.gov/ttn/amtic/airtox.html]).