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RCRA TESTING TECHNIQUES

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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FROM: David Friedman, Chief
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TO: Addressees

This memo will address the following topics:

- o GC/MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes
- o Notes on Safety in the Laboratory
- o Standardization of Method 8610, Part 2
- o 1988 Solid Waste Testing and Quality Assurance Symposium
- o TCLP Video
- o Application of Structural Integrity Procedure when Performing EP Analyses

GC/MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes

The RCRA list of toxic compounds (Appendix VIII) contains over 300 organic analytes. In response to a petition by the state of Michigan, the Agency proposed to add over 100 additional organic compounds to the list. In order to develop and validate methods for the analysis of these compounds in wastes, EP extracts, and ground water, the Environmental Monitoring and Support Laboratory in Cincinnati (EMSL-CI) has been evaluating applicability of Methods 8240 and 8270 for these analyses.

The first phase of this approach involved the identification of those compounds which are amenable to GC separation and MS detection. These evaluations involved the analyses of solutions of standard materials using the GC/MS conditions described in the Contractor Laboratory Protocol (CLP) for the application of Methods 8240 and 8270 for volatile and semi-volatile organic compounds, respectively.

EMSL-CI recently issued the first report on this study. The report describes the procedures and presents the results obtained from this first phase of the study. The compounds were classified as candidates for Method 8240 or METHOD 8270 testing. Some compounds were not tested because they fell into one of the following categories:

- o The chromatographic behavior of the compound had already been thoroughly characterized.
- o The compound was known to degrade rapidly in aqueous sample matrices.
- o The compound was known not to be amenable to gas chromatography -- Compounds known to be too polar and/or too thermolabile to elute using Method 8270 conditions.
- o Standards were not available, either from the EPA repository or from commercial sources, for the compound.

For compounds not excluded for the above reasons, the following data were obtained:

- o GC Performance -- retention characteristics.
- o Mass Spectral Performance -- response factors, key ions for detection and quantification using extracted ion current profiles (EICP).

The project demonstrated that of the Appendix VIII or Michigan List analytes tested, 64 are compatible with the GC/MS analysis for volatiles and 220 others can be detected using the Superfund GC/MS program for semi-volatiles.

Notes on Safety in the Laboratory

The items below were brought to our attention and we felt it would be of benefit to reprint them in this issue. Chemical Safety (C&EN, July 27, 1987)

Noxious Fumes From Nitric Acid Digestion

SIR: We were interested to read of Paul Haas' description of an unexpected reaction involving the acidification of hydrous metal oxides with nitric acid (C&EN, April 20, page 3). The health and environmental chemistry group at Los Alamos National Laboratory conducts the extraction procedures-toxicity tests for determination of metals in hazardous waste materials as required by the Environmental Protection Agency. Because of the nature of these materials, there is always an inherent amount of uncertainty with each sample to be analyzed. However, our experience has shown that approximately one third of all samples are likely to yield a fairly vigorous reaction at some point throughout the extraction procedure.

Recently, we experienced an incident involving one of these samples. A sample aliquot was being prepared for mercury analysis by the stepwise addition of digestion acids and potassium permanganate. Nitric acid had been added to the aliquot in a 100-mL Erlenmeyer flask and the mixture had been allowed to stand for 15 to 20 minutes with occasional swirling. An ice bath was used to douse vigorous reactions. The flask was then removed from the hood and placed in the laboratory sink, which contained approximately 1 inch of cool water. Shortly thereafter, a reddish-brown mist containing probable fumes of nitrogen dioxide and butyric acid (based upon the appearance and odor) was liberated from the flask, resulting in mild exposure to the employee conducting the analysis. Several other individuals in the building also reported nausea and slight dizziness.

At the time of removal of the flask from the laboratory hood, the sample appeared quiescent; it was removed from the hood in order to make room for other samples being prepared in a similar fashion. In the future, all such samples will be retained in the hood throughout the procedure at the possible cost of increasing throughput time for sample analyses.

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Standardization of EPA Method 8610, Part 2

Method 8610, "Total Aromatics by Ultraviolet Absorption" was evaluated in conjunction with Method 3560, "Reverse Phase Cartridge Extraction" for the separation and semi-quantitative determination of visible or ultraviolet absorbing organic compounds listed in Appendix VIII. In Part 1 of this program, reported on earlier by EMSL-CI (EPA/600/S4-85/052), the following work was conducted:

- o A data base of visible and ultraviolet (UV) spectral data for the Appendix VIII compounds was developed and used to estimate detection limits for those compounds which absorb UV or visible light in the region 220 to 700 nm.
- o The reverse phase cartridge extraction procedure of Method 3560 was evaluated and modified for the separation of polar and non-polar subsets of 21 Method 8610 analytes using methanol hexane eluents. However, the extraction procedure was found to be unsuitable for analyzing the tested composite groundwater sample. The tested water contained five sediment particles which partially moved through the extraction cartridge and possibly interfered with the UV analysis.
- o The spectrophotometric determinative technique of Method 8610 was evaluated and found, in the range of 220 to 400 nm, to be very sensitive for a majority of the compounds.

Based on these results, further work was conducted by EMSL-CI to further investigate the applicability of these methods in a variety of ground-water samples and to refine method detection limit estimates.

Seven ground-water samples were supplied for the study by ASTM Committee D-34 members. These samples were evaluated for background UV absorbance, and duplicate sample extractions were used to simulate down-gradient versus upgradient testing. An estimated positive response decision level was found to be 0.02 absorbance units. Five Method 8610 analytes were evaluated for spike recoveries from both reagent water and a composite ground-water sample. One analyte was found to be unstable in water and the elution solvents used. The remaining four analytes had good total recoveries from reagent water ranging from 79 to 108 percent with standard deviations of all but one analyte ranging from 1 to 5 percent. Spike recoveries for composited ground water were not reproducible due, apparently, to a significant variability in recovery of native UV absorbing material. The cause of the variability could not be specifically attributed to, but may have been associated with, the presence of very finely divided particulate material.

Microwave Oven Safety

It has recently come to our attention that several laboratories are using kitchen type microwave ovens to aid in the acid dissolution of solid and liquid waste samples. The Methods Section is currently evaluating commercial microwave oven assisted sample digestion procedures and hopes to recommend certain approaches in the near future. Those laboratories now using or contemplating the use of kitchen type ovens should be aware of several significant safety issues. First, when acids such as nitric and hydrochloric acids are used to assist sample digestion in open vessels, or in sealed vessels equipped with venting features, the potential for the acid gases released to corrode the safety wiring that prevents the microwave magnetron from shutting off with the door open. This can result in operator exposure to microwave radiation. On at least one occasion this has resulted in a severe burn to a laboratory technician. Use of an oven with corrosion resistant safety wiring may prevent this from occurring.

The second safety concern relates to the use of sealed containers in the oven. It has been found that pressure, coupled with elevated temperature and the acid matrix is more effective in dissolving certain samples than either of these separately. However, many commonly used digestion vessels constructed from fluorocarbons may crack, burst, or explode in the oven under certain conditions. Only a few containers are considered acceptable at present. In addition, pressure buildup may be exacerbated by use of certain acids such as perchloric which decompose under certain pressures and temperatures to form gaseous byproducts.

1988 RCRA/CERCLA Symposium

We are again requesting your suggestions for papers and poster presentations for the 1988 Solid Waste Testing and Quality Assurance Symposium. It is scheduled for July 11-15, 1988 and will cover the areas of physical, chemical and biological testing, quality assurance, sampling, hazardous waste identification, enforcement, laboratory information management and any other topics that are of interest to State, Regional, private sector, and contract laboratories. This year we plan to offer training classes in quality assurance/quality control, and statistics. Denise Zabinski will be accepting your suggestions and can be reached on 202/382-4761 or FTS 382-4761.

TCLP Video

Each Regional Quality Assurance Officer has received 2 copies of the new Toxicity Characteristic Leaching Procedure

(TCLP) video to be used both for in-house training and to serve as a lending library. For those of you who would like to purchase the video instead of borrowing it from a QAO, it is available for \$40 from the American Public Works Association (APWA) in Chicago. Please contact Dan Hansen of APWA at (312) 667-2200 for further information.

Applicability of the Structural Integrity Procedure When Performing Extraction Procedure Toxicity Determinations

Recently a question came in regarding whether or not one could use the Structural Integrity Procedure (SIP) when evaluating a certain waste in lieu of grinding the waste prior to performing the extraction. Since this was not the first time we have received such questions, I felt it would be appropriate to review when use of the SIP is appropriate and when it should not be used.

The Extraction Procedure (Method 1310) protocol requires that wastes be ground to pass a 9.5 mm sieve unless the waste is in the form of a single piece (Step 7.9). If the waste consists of a single piece, or if upon disposal will be in the form of a single piece, then one may use the SIP in lieu of grinding. The SIP may, therefore, only be used to evaluate a waste that is in the form of a monolithic mass. In addition, in order for the sample, being tested, to be truly representative of the waste as a whole, the waste will have to be homogeneous. Put another way, one must be able to obtain a cylindrical sample of the waste with the dimensions 3.3 cm X 7.1 cm which has the same composition and properties as the waste as a whole. Thus when determining whether one can use the SIP the critical questions to be answered are:

1. Is the waste a monolithic block when disposed of, and
2. Is the waste homogeneous.

To be considered a monolithic mass, the waste must be produced or generated in the form of discrete units of material. For example, a solidified waste may be cast into cylinders or blocks of a predefined size and shape; the waste may be emplaced in a landfill cell as a fast setting liquid which then hardens into a mass the shape of the cell (a la concrete poured into a form); or the waste may be a product that is in the form of a discrete unit (e.g., telephone pole, block of plastic). A material, however, that, while at some point in the production process is in the form of a monolithic mass, randomly breaks up as a consequence of its management prior to disposal would not be considered to be a monolithic waste and therefore is not a candidate for testing using the SIP. It should be noted that, while wastes are normally tested using the SIP at the time of generation, pozzolonic or other wastes that "set up" with time to form a solid mass may be aged for up to 30 days before

testing (see Method 1310 Step 7.10.1).

The second critical parameter that must also be considered is whether the waste is homogenous. In order for the sample that is to be tested to be a representative sample, the waste from which the sample is being derived must be homogeneous. If the waste is not homogeneous the subsample used in the SIP would not be representative. Examples of non-homogeneous wastes are batteries and hazardous wastes encapsulated in a plastic or other covering to prevent contact between ground water and the waste. These wastes are considered not to be homogeneous since the outer surface is different from the inner surface, and a small sample of the waste cut from the larger block of waste would not have the same properties (i.e., composition, permeability) as that of the "whole waste". If, however, the waste was prepared, by a fixation process, in the form of cylinders 3.3 cm X 7.1 cm, the samples would be representative of the waste as a whole and could be tested using the SIP.