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RCRA METHODS AND QA ACTIVITIES (NOTES)

MEMORANDUM #6

DATE: April 1985

SUBJECT: Notes on RCRA Methods and QA Activities

FROM: David Friedman, Manager
Methods Program (WH-562B)

TO: Addressees

Thank you again for your response to my previous RCRA Methods and QA Activities memos. In this memo we will inform you about the following recent initiatives in the Agency:

- o Public Meetings on Delisting
- o Intra-agency Work Group on Update to SW-846
- o Development of New Testing Methods and Reevaluation of Existing Methods

We appreciate your comments and suggestions.

Public Meetings on Delisting

Approximately 200 persons attended public meetings in Washington, D.C. and Dallas, Texas, organized by the Delisting Program. The meetings were conducted to describe in detail how future delisting petitions will be affected by the Hazardous Waste Amendments of 1984 and to provide instruction to petitioners on the preparation of supplemental material that should be included in future delisting petitions. Presentations were made on the reauthorization of RCRA, the general petition review process, information resources and special procedures that will apply to petitions concerning wastes from petroleum refineries and multiple waste treatment facilities. A discussion session followed the presentations in which attendees were given

the opportunity to question the delisting staff about their particular concerns.

Intra-agency Work Group on Update to SW-846

As part of the process of finalizing the October 1, 1984 proposal to update SW-846, "Test Methods for Evaluating Solid Waste," an intra-agency work group is in the process of considering the comments received by the Agency in response to the proposed changes and is rewriting some of the methods to reflect these comments and suggestions. OSW expects to complete this process by the end of this summer, with Federal Register publication anticipated in the Spring of 1986.

Development of New Testing Methods and Reevaluation of Existing Methods

As part of its efforts to develop new testing methods and to determine the accuracy, precision and sensitivity of the existing methods, the EPA Office of Research and Development has completed a number of test methods studies including:

- Method 9022 and Interim Method 450.1 -- Determining total organic halide (TOX) in ground water and waste oil

- Method 8030 -- Determining acrolein, acrylonitrile and acetonitrile in ground water, solids and organic liquid matrices

- Method 8090 -- Procedure for analysis of nitroaromatics and cyclic ketones in ground water, liquid waste and solid sample matrices

- Method 8280 -- Procedure for analysis of hazardous wastes containing tetra-, penta- and hexa-chlorinated dibenzodioxins and -furans

- Application of a gas chromatography/Fourier transform infrared protocol to the determination of semivolatile organic compounds in waste water, soils, sediments and solid wastes

- Analytical methods for compounds that do not gas

chromatograph.

The following sections describe these recent research developments.

Method 9022 and Interim Method 450.1

Various methods for determining total organic halide (TOX) in samples of ground water and waste oil were evaluated by EMSL-CIN (Thomas Pressley, 513-684-7494). Of three inorganic halide species generation approaches and three inorganic halide determinative techniques evaluated for ground water analyses, one combined approach using Schoeniger flask oxidation with colorimetric chloride determination was chosen for laboratory validation and method detection limit studies. Ground water samples were also analyzed for TOX using neutron activation analysis (Method 9022).

The results of this evaluation indicate that Method 9022 is an appropriate technique to TOX analysis and offers the additional advantage of providing individual chlorine and bromine values for the samples at levels equal to TOX detection limits achievable with the microcoulemetric determinative technique which as a reliable limit of sensitivity at 5 ug/L (Interim Method 450.1). The Schoeniger flask/colorimetric chloride and neutron activation analysis methods were found to give TOX results for spiked ground waters that were comparable to those obtained using the microcoulometric method. However, the Schoeniger flask/colorimetric halide method was useful only for halide levels above 0.2 mg/L due to the high halide background levels encountered in the reagents.

A method for analysis of oil samples that uses the sodium biphenyl reagent and a colorimetric chloride method was found to be unsatisfactory for the analysis of various oils spiked with PCBs due to interferences in the colorimetric determinative step that resulted in recoveries greater than 100 percent. Further evaluation of the sodium biphenyl reagent using alternative determinative techniques, such as microcoulometric detection or an additional clean-up step for the extract prior to the colorimetric determinative step, will have to be performed to establish the usefulness of the technique at halide levels in the range of 20 to 350 ug/g.

Method 8030

Method 8030 was modified using revised chromatographic conditions for determining acrolein, acrylonitrile and acetonitrile in ground water, solids and organic liquid matrices. In order to evaluate these modifications, method validation studies were conducted on each of the four sample preparation techniques included in Method 8030, namely: (1) heated purge-and-trap; (2) polyethylene glycol (PEG) extraction followed by heated purge-and-trap; (3) direct liquid injection; and (4) manual heated headspace. Each method validation involved the determination of the method detection limit (MDL) and seven replicate analyses of one or two matrices unspiked and spiked at two different levels. Ground water was analyzed by the heated purge-and-trap method; a solid waste was analyzed by the PEG/heated purge-and-trap method; and a liquid organic waste was analyzed by direct liquid injection and by the heated headspace method.

The heated purge-and-trap method gave excellent recoveries (85 to 96 percent) and precision for the three analytes in ground water. The PEG/heated purge-and-trap method gave good recoveries (76 to 96 percent) for acetonitrile and acrylonitrile in the solid waste but poor recoveries for acrolein (10 percent). Problems resulting from residual amounts of PEG indicated that additional modifications of this method are needed. The direct liquid injection technique gave excellent results for the determination of all three analytes (86 and 111 percent recoveries) in the liquid organic waste; however, late eluting material may present serious problems in some cases. The manual heated headspace method gave distinctly less accurate and less precise results than the PEG/purge-and-trap method for the determination of acetonitrile and acrylonitrile in the solid waste sample. Acrolein was not recovered at all by the method due, apparently, to decomposition during the one-hour equilibration at 90°C. The headspace method gave extremely erratic results for the analysis of the organic liquid waste and was, therefore, considered completely unsatisfactory for such samples.

This study was conducted by the EMSL-CIN laboratory (James Longbottom, 513-684-7308).

Method 8090

Another study recently completed by the EMSL-CIN laboratory (James Longbottom, 513-684-7308) was a single laboratory evaluation of Method 8090, which is a procedure for the analysis of nitroaromatics and cyclic ketones in ground water, liquid waste and solid sample matrices. The method spike recoveries in authentic matrices at two challenge concentrations were determined. Authentic matrices were obtained from industrial sources with manufacturing processes that might require the use of this method for monitoring, and as such these authentic samples provided the analytical conditions and background interferents that might be expected in actual implementation of this method. The method detection limit (MDL) in reagent water for all the analytes ranged from 1.2 ug/L to a low of 0.26 ug/L. The experimental method detection limits were lower than the published method detections in Method 8090 for 2,4-dinitrotoluene, 2,6-dinitrotoluene, nitrobenzene and isophorone. The recoveries for all the analytes in reagent water were greater than 75 percent.

The recoveries for the majority of the analytes in the three matrices (ground water, nonaqueous liquid waste, and solid waste) were generally good. All the analytes gave good recoveries (greater than 70 percent) and good precision (relative standard deviation less than 12 percent) in the ground water matrix. 2,4-Dinitrotoluene, 2,6-dinitrotoluene, 1,3-dinitrobenzene and 1,4-naphthoquinone gave good recoveries (greater than 70 percent) in the nonaqueous liquid waste. Poor recoveries were observed for nitrobenzene and isophorone in the nonaqueous liquid waste. For the solid waste matrix, 4,4-naphthoquinone gave the worst recover (50 percent) of the six analytes, while the remaining analytes gave recoveries ranging from 60 to 70 percent at the high concentration level and greater than 80 percent at the low concentration level.

Method 8280

In 1983, EPA proposed a ruling affecting disposal of hazardous wastes containing tetra-, penta-, and hexa-chlorinated dibenzodioxins and -furans. As a result, the EMSL-LV laboratory initiated a validation study of the method proposed to detect these substances.

The RCRA Method 8280 consists of four major sections: (1)

extraction of the analytes from the environmental sample; (2) "open" chromatographic clean-up with alumina using methylene chloride/hexane eluent; (3) MPLC clean-up; and (4) analysis by capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS). In order to test Method 8280 efficiently and to develop appropriate modifications with minimal effort, each section of the methodology was tested separately. Initial tests were performed on a simple (pottery clay soil) sample matrix and upon standard solutions. Necessarily, the first step evaluated was the measurement technique. Both GC/MS and GC/EC (electron capture detection) were tested using guidelines from the published RCRA method. Because the analytes could not be measured at the published mass-to-charge ration (m/z) values by GC/MS, these values were corrected prior to further work.

In summary, the following revisions were made to the published method: (1) correct m/z values were substituted for those in the published method so that the mass spectrometer could detect analytes and standards introduced via the interface gas chromatograph; (2) the extract clean-up with an alumina column was revised so that all desired analytes eluted in a single fraction, with the bulk of the analytical interferences removed; (3) the method was revised so that wet samples could be accommodated; and (4) NPLC procedures that could be performed effectively and be reproduced consistently were developed. The extraction revision allows accommodation of wet samples and improves recovery of spiked analytes in dry soil samples.

The RCRA method with revisions discussed above was subjected to performance tests that included: (1) analysis of reference materials containing 2,3,7,8-TCDD and interferences; and (2) precision and accuracy determinations on samples having known composition through spiking the sample matrix at this laboratory.

Two independent teams of analysts investigated the performance of the revised method using precision and accuracy determinations (standard deviation of results) and by recovery of spiked analytes and isotopically labeled standards. Effect of experimental parameters, such as QC column type (coating) and alumina activation level were also determined.

After incorporating necessary revisions, satisfactory method performance has been demonstrated on soil-type samples. Much

precision and accuracy data obtained to date were based on GC/EC determinations. Comparisons to the precision and accuracy attainable by NPLC/LRMS is underway. Performance of the method on relatively complex matrices, such as sludges, still bottoms and fly ash was determined.

Although the method was found suitable for soils, fly ash and other relatively clean matrices, serious interferences were obtained during the analysis of still bottoms. Additional clean-up steps are now being studies. A copy of the revised method will be attached to the July memo (Ron Mitchum, 702-798-2103).

Gas Chromatography/Fourier Transform Infrared

The application of gas chromatography/Fourier transform infrared (GC/FT-IR) data to regulatory decisions requires the availability of validated analytical protocols. A GC/FT-Ir protocol was developed by EMSL-LV (Donald Gurka, 702-798-2113) that is applicable to the determination of semivolatile organic compounds in waste water, soils, sediments and solid wastes. The protocol is designed for automated analysis of multicomponent environmental and hazardous waste extracts. Waste water analysis for semivolatile organic compounds is based upon extracting l L of sample with methylene chloride and concentrating the sample extract to 1.0 mL. The analysis of the semivolatile fraction derived from solid waste analysis is based upon extracting 50 grams of sample and concentrating the sample extract to 1.0 mL. A gel permeation option is included to further purify those extracts which cannot be concentrated to the specified final volume.

Using capillary GC/FT-IR techniques, waste water identification limits of 150 to 400 ppb can be achieved with this method while the corresponding identification limits for solid samples are 3 to 8 ppm. Automated packed column GC/FT-IR identification limits are approximately a factor of five higher than the corresponding capillary GC/FT-IR values. The most frequent obstacle to achieving these identification limits is expected to be the presence of large quantities of interfering high boiling coextractants. These coextractants would raise the identification limits by preventing the concentration of extracts to the desired final volume, thereby necessitating gel permeation clean-up, and/or by decreasing the spectral signal-to-noise GC-volatile analytes by raising the spectral background intensity.

Triple Quadrupole Mass Spectroscopy

In order to develop analytical methods for compounds that do not gas chromatograph, EMSL-LV (Steve Billete, 702-798-2232) has been studying the use of alternative analytical methods. A number of dye compounds and dye wastes were characterized by MS/MS using thermospray ionization and triple-quadrupole mass spectrometry. The polymethine, commarin, xanthene, arylmethane and non-sulfonated azo compounds are classes of dyes that, in general, give collision mass spectra when introduced into the spectrometer via the thermospray interface without chromatography. Other classes of dyes, such as phthalocyanines, stilbence and benzidine dyes, have not been detected by this method.

Many synthetic intermediates and other dyes were detected in standards of individual dyes. The precursor compounds are generally not completely removed from the commercial product. The dyestuffs are formulations based on color index standards. Dye wastes (mother liquors from various dye processes) were analyzed without pretreatment before injection into the spectrometer. High percentages of the starting materials used in the synthesis of specified dyes were often detected. Other types of dyes spiked into these wastes could be identified by their collision spectra. The quantification of these dyes proved difficult because of the impurity of the dye standards.

Detection limit studies indicate that at least 100 mg to 250 mg of injected material are needed for the dye to be identified. However, specific detection limits are dependent upon the class of dye and its actual chemical structure.

The use of triple-quadrupole mass spectrometry proves very effective in identifying those dyes that undergo thermospray ionization. The production of a useful spectrum from the single ion per compound generated from thermospray ionization makes the triple-quadrupole mass spectrometer useful in both structure and mixture analysis.

Test Methods Discussed at AOAC Meeting in Dallas

In addition to the above studies for which reports have recently been completed, two other methods under development, a new Toxicity Characteristic Leaching Procedure (TCLP) and a

Sorbent Pressure Test Method, were discussed at a session of the AOAC meeting on April 11, 1985 in Dallas, Texas. A discussion of these new methods is presented in the following sections.

Toxicity Characteristic Leaching Procedure

The 1984 amendments to the RCRA call for EPA to make the Extraction Procedure (EP) more accurate and to expand the hazardous waste characteristics. In response, the Agency is expanding the list of compounds that can be detected using the Extraction Procedure and is developing a second generation mobility procedure. The new TCLP is being designed to be suitable for determining the leaching behavior of volatile compounds as well as to be less costly and more precise than the current EP. Furthermore, the features of this new procedure are expected to approximate the leaching action of a sanitary landfill. The draft TCLP that was discussed at the AOAC meeting in Dallas makes the use of a zero-headspace extraction vessel, the tumbler type agitator currently employed in the EP, and an acetic acid/sodium acetate buffer as the extraction medium. A report is in preparation summarizing the results of the lysimeter and laboratory experiments that led to the draft procedure. A copy of the draft method is attached. For further information, contact Todd Kimmell 202-382-4795).

Sorbent Pressure Test Method

Compression of materials occurs during routine landfill operations, and the 1984 amendments to RCRA directed EPA to prohibit the landfill disposal of liquids absorbed in materials (sorbents) which can release these liquids when compressed.

In order to determine whether certain sorbents could release liquids under simulated landfill pressure, the Agency has initiated a program to develop a new test method, entitled the Sorbent Pressure Test. As discussed at the AOAC meeting, centrifugation and consolidation are currently being investigated as a means of simulating landfill pressure. The test will be designed to be easily applied in the field and to yield both qualitative and quantitative results.

Attachment