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MEMORANDUM #7

RCRA METHODS AND QA ACTIVITES (NOTES)

DATE: June 30, 1985

SUBJECT: Notes on RCRA Methods and QA Activities

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

TO: Addressees

Today's memo will cover the following subjects:

Metal Determination in Ground Water

Dioxin Method 8280

Performance Audits on Gas Samplers

Validation of Method 3540

Reactivity Test Methods

Symposium of Solid Waste Testing and Quality Assurance

Thank you for past comments and suggestions.

Metal Determination in Groundwater

The forthcoming publications, "Ground Water Technical Enforcement Document" (OWPE) and the Third Edition of SW-846, will provide greater detail on how metals are to be determined in ground water. The following policy will be implemented in both documents.

> All ground water samples are to be analyzed for total recoverable metals (unfiltered, mild digestion) and dissolved metals (filtered, mild digestion) as defined in the EPA publication "Methods for Chemical Analysis of Water and Waste" (EPA 600/4-79-020), Section 200

Metals, paragraphs 3.7 and 3.4. Total recoverable metals and dissolved metals are to be determined by the methods given in the same publication in Section 200 Metals, paragraphs 4.1.4 and 4.1.1. (The digestion given in Note 3 of 4.1.1 is always to be used for ground water samples.)

Organic determinations are to be made only on ground water samples that have not been filtered.

An on-site filtration method will be developed and evaluated before inclusion in SW-846.

Dioxin Method 8280

The single laboratory evaluation of Method 8280 for analysis of halogenated dibenzo-p-dioxins and dibenzofurans has been completed. The method consists of extraction, base and acid washes, alumina column chromatography, reverse phase HPLC, carbon column chromatography and quanititation by high resolution gas chromatography low resolution mass spectrometry (HRGC/LRMS) (see Table I). Analyses, concentrations and performance data are given in Table II. Detection limits derived from the single lab study are given in Table III. These may be higher than lowest possible detection limits because calculations are based on high natural and spiked dioxin concentrations. The EMSL-Las Vegas laboratory is currently investigating method modifications aimed at lowering the detection limits and is preparing for a multi-laboratory evaluation of the current method.

Availability of PPB Hazardous Organic Cylinder Gases for Performance Audits

In order to minimize the chance of poor data being collected when performing trial burns and other combustion process monitoring, the EMSL-RTP laboratory has prepared several audit cylinders for use in performing performance audits of SW-846 sampling methods 1.2.1.8 (VOST) and 1.2.1.13 (MM5). These multicomponent organic cylinder gases have been successfully used in audits during RCRA hazardous waste trial burns.

As a result of the success with these cylinders, OSW believes it is prudent for all persons performing such sampling to use a cylinder audit during each sampling episode. If such a

level of Quality Assurance cannot be performed, then cylinder audits should be performed during all trial burns. The cylinder gas audit can be used for all volatile organic sampling that uses either the VOST or bag techniques. The audit adds an important ingredient now missing from such trial burns--assessment of sampling accuracy. Currently, EPA and State personnel who require trial burns for POHC have little means of knowing the accuracy of POHC measurements. Requiring permit applicants to conduct cylinder audits during the trial burn adds an important weapon to the QA arsenal. OSW strongly recommends instituting this requirement weapon to the QA arsenal. OSW strongly recommends instituting this requirement.

These cylinders are available, at no cost, from the EMSL-RTP laboratory. Each audit cylinder contains 5 to 9 hazardous organics. Audit cylinders are available in two concentration ranges. The concentration of each hazardous organic in the low audit cylinders is between 7 and 90 ppb. The concentration of each hazardous organic in the high audit cylinders is between 90 and 430 ppb. Groups I and II cylinders are currently available for audits. Group III cylinders will be available in the Fall, 1985. Groups I, II and III cylinders contain the following hazardous organics:

Group I Cylinders	Group II Cylinders	Group III Cylinders
Carbon tetrachloride	Trichloroethylene	Pyridine
Chloroform	1,2-Dichloroethane	Vinylidene chloride
Perchloroethylene	1,2-Dibromoethane	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon-113)
Vinyl chloride	Acetonitrile	
Benzene	Trichorofluoromethane (Freon-11)	1,2-Dechloro-1,1,2,2-tetrafluoroethane (Freon-114)
	Dichlorodifluoromethane (Freon-12)	Acetone
	Bromoethane	1,4-Dioxane

Methyl ethyl ketone	Toluene
1,1,1-Trichloroethane	Chlorobenzene

All audit cylinders are periodically analyzed to assure cylinder concentrations have remained stable. Also, all stability analyses in Appendix A include quality control analyses of ppb hazardous organic gas standards prepared by the National Bureau of Standards for EMSL-RTP/QAD.

Audit cylinders may be obtained by contacting:

Robert L. Lampe
USEPA, Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711
Telephone: Commercial (919) 541-4531 or FTS 629-4531

Validation of Method 3540

The development and evaluation of fortification/ homogenization procedures for preparing uniform distributions of analytes in diatomaceous earth showed no appreciable differences between fortification solvents, between mechanisms of homogenization, or between duration of homogenization. Uniformity of distribution of analytes in the diatomaceous earth was essentially independent of the parameters. Consequently, the most facile approach (i.e., fortifying using methylene chloride followed by tumbling for 30 min) was applied to subsequent experiments.

The evaluation of the Soxhlet Extraction Procedure (Method 3540, SW-846) using reagent diatomaceous earth demonstrated that this procedure provides accurate and precise measurements on nonvolatile components. Recoveries of such species from fortified diatomaceous earth was approximately 85 percent, with relative standard deviations of less than 11 percent. Recoveries of the three volatile analytes, toluene, p-xylene, and o-xylene were considerably lower (-40%). Loss of these volatile compounds during evaporation of gross solvent in the fortification step was considered the most probable cause of this poor performance. Extraction and K-D evaporation were also minor contributors. No effect of using diatomaceous earth from different sources on recovery of target analytes was noted.

Precision of determination of unknown components of diatomaceous earth fortified with actual pesticide industry waste was somewhat lower (approximately 27% RSD). This observation was attributed to the difficulty of homogenizing a mixture of two solid materials.

Reactivity Test Methods

Development of reactivity test methods for those waste materials which are capable of detonation is underway. In an interagency agreement with the Bureau of Mines Laboratory (BOM) in Pittsburgh, Pennsylvania, OSW sponsored a study that evaluated the U.S. Card Gap Test and the U.S. Internal Ignition Test as tools for determining if a given waste is an explosive that could undergo detonation under reasonable mismanagement conditions. Samples of sludge from several explosives processing waste treatment facilities were collected and analyzed as well as a series of standard explosives for calibration use. Because of the inconclusive nature of the results of the BOM work, further evaluation is needed before any decision is reached as to the applicability of these tests to RCRA wastes.

In the interim, OSW has supported the use of a battery of tests to determine reactivity due to explosive properties. This battery is outlined in a test plan submitted by the U.S. Army.

Please contact Florence Richardson (FTS 382-4770) for additional information on the aspect of reactivity.

TABLE I. FLOW SHEET FOR METHOD 8280 DIOXIN ANALYSIS

1 - 10g Sample

MeOH:Pet. Ether:H2O (1:4:5) used

Extract ≥ 100 ml for Ash; Toluene used for Activated

≥ Carbon; MeOH:H2O (7:3) used for soil.

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≥

≥ Aqueous

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≥

Discard

Organic

Wash with

≥ 20% KO? (Upside "R")

≥

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Aqueous Organic

Wash with

Discard ≥ conc. H2SO4

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Aqueous Organic

Alumina Column (3g)

Discard ≥ Clean up

≥

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Fraction 1 (MeC12%Hexane (20:80) Fraction 2 (MeC12%Hexane (50:50)

≥ ≥

≥ ≥

Discard HPLC Cleanup

≥ C18-Reverse Phase

≥ (Isocrate-MeOH)

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Fraction 2 Fraction 1

≥

≥ Discard

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Soils Sludge

Fly Ash Tars

(HRGC/LRMS) Still Bottoms

Carbon Column

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≥ Carbon PX-21 (Amoco Res)

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Fraction 1 and 1 Fraction 3 (Toluene)

Discard HRGC/LRMS

 TABLE II. PRECISION DATA FOR REVISED METHOD 8280

Compound	Matrix	Analyte Level Native + Spike (ng/g)	N	Mean Percent Recovery	Percent RSD
1,2,3,4,7-PeCDD	clay	5.0	4	58.4	3.36
	soil	25.0	4	62.2	8.92
	sludge	125	4	79.2	6.93
	fly ash	13.9	4	102.4	10.3
	still bottom	2500	2	81.8	--
1,2,3,7,8-PeCDD	clay	5.0	4	61.7	23.2
	soil	25.0	4	68.4	10.8
	sludge	125	4	81.5	5.28
	fly ash	46	2	104.9	--
	still bottom	2500	2	84.0	--
1,2,3,4,7,8-HxCDD	clay	5.0	4	46.8	28.9
	soil	25.0	4	65.0	12.9
	sludge	125	4	81.9	9.0
	fly ash	46	2	125.4	--
	still bottom	2500	2	89.1	--
1,2,3,4,6,7,8-HpCDD	clay	5.0	4	ND	--
	soil	25.0	4	ND	--
	sludge	1 x 104	8	--	--
	fly ash	--	-	--	--
	still bottom	--	-	--	--
2,3,7,8-TCDD (C-13)	clay	5.0	4	64.9	7.58
	soil	25.0	4	78.8	9.14
	sludge	125	6	78.6	3.42
	fly ash	5.0	4	88.6	6.74
	still bottom	2500	3	69.7	7.47
1,2,7,8-TCDF	clay	5.0	4	65.4	6.91
	soil	25.0	4	71.1	8.40
	sludge	125	4	80.4	3.08
	fly ash	3.7	4	90.4	11.1
	still bottom	2500	2	104.5	--
1,2,3,7,8-PeCDF	clay	5.0	4	57.4	5.18
	soil	25.0	4	64.4	6.77
	sludge	125	4	84.8	9.74

	fly ash	46	2	105.8	--
	still bottom	178,000	2	--	--
1,2,3,4,7,8-HxCDF	clay	--	-	54.2	--
	soil	25.0	4	68.5	10.0
	sludge	133	4	82.2	5.29
	fly ash	17.6	4	91.0	8.71
	still bottom	2500	2	92.9	--

TABLE III. DETECTION LIMITS (ppb) FOR RCRA METHOD 8280

Analyte Class	Clay	Soil	Fly Ash	Still Bottom	Sludge
TCDD	1.0	5.0	1.0	500	25
TDCF	0.5	2.5	0.5	250	12
PeCDD	1.5	7.5	1.5	750	38
PeCDF	1.0	5.0	1.0	500	25
HxCDD	2.0	10	2.0	1000	50
HxCDF	1.5	7.5	1.5	750	38