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Project Summary

Single-Laboratory Validation of EPA Method 8150 for the Analysis of Chlorinated Herbicides in Hazardous Waste

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A single-laboratory validated analytical protocol is described, which is applicable to the determination of the herbicides Dicamba, Silvex, 2,4-D, 2,4-DB, 2,4,5-T, Dinoseb, MCPP, and MCPA in hazardous waste extracts. The method consists of herbicide hydrolysis followed by diazomethane esterification and subsequent determination of the herbicide methyl esters by capillary column gas chromatography with electron capture detection (GC/EC). An electron impact gas chromatography/mass spectrometric (GC/MS) confirmation of the GC/EC results is included.

The protocol validation procedure consisted of (1) ruggedness testing, (2) simplex optimization of key experimental variables, and (3) the determination of extraction recoveries, detection limits, and the GC/EC linear dynamic range for each herbicide methyl ester. This protocol, which employs a single fused silica capillary column separation for all the target methyl esters, is a significant improvement over all earlier gas chromatographic (GC) procedures, each of which utilizes three different packed GC columns. The method, however, was inapplicable to Dalapon, which eliminates hydrogen chloride during the sample workup.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The United States Environmental Protection Agency (EPA) is currently involved in a program to determine the accuracy and precision of key EPA analytical protocols. As part of this program, the Office of Solid Waste (OSW) is validating the protocols in its Manual SW-846 *Test Methods for Evaluating Solid Waste*. Included in Manual SW-846 is Method 8150 for the determination of chlorinated herbicides, which is based on earlier American Society for Testing Materials (ASTM) and EPA procedures for determination of herbicides in water. Method 8150, therefore, required validation for its applicability to solid wastes.

Guidelines to aid in validating analytical procedures have been published by ASTM and by the Association of Official Analytical Chemists (AOAC). In addition, a step-by-step protocol for the validation process has recently been published (JAOAC, *66*, 455, 1983).

The following work plan was utilized for this method validation:

1. Evaluate the original analytical protocol for Method 8150 as published in Manual SW-846.
2. Locate key method variables by ruggedness testing using Youden's approach.

3. Optimize key method variables using the simplex optimization technique.
4. Using the EPA format, prepare a detailed analytical protocol for the optimized method.
5. Determine the linear dynamic quantification range for each target methyl ester.
6. Determine the percent extraction recovery for each target methyl ester.
7. Prepare a GC/MS confirmation technique for the optimized GC/EC method.
8. Test the analytical protocol on spiked extracts of hazardous waste samples.
9. If sample results indicate procedural problems, revise the analytical protocol, as necessary.

Conclusions and Recommendations

A single-laboratory validated protocol for determination of herbicides in hazardous waste has been prepared. This protocol is applicable to the determination of 9 of the 10 Method 8150 target methyl herbicides. The exceptional ester is Dalapon, which decomposes during the sample workup. Final ruggedness testing on the optimized protocol for the 9 methyl esters yielded a mean recovery of 89.3 percent with a mean standard deviation of 4.3 percent for 20 determinations. The GC/EC linear dynamic range exceeded two orders of magnitude for MCPP and MCPA and three orders of magnitude for the 7 target esters. Detection limits were in the ppm range for MCPP and MCPA and in the low ppb range for the other herbicides. These detection limits and linear dynamic ranges reflect the wide span of the target compound GC/EC response factors. Although these detection limits are adequate for hazardous wastes, which typically contain ppm and higher contaminant levels, we recommend that appentafluorobenzyl GC/EC procedure be evaluated for its applicability to low-level environmental samples.

Results and Discussion

The original Method 8150 protocol was modified to use a single, 20-minute, fused silica capillary column GC run for all target herbicide esters. This modification yields substantial savings in GC/EC data acquisition time over the three packed GC columns specified in Method 8150. Methylene chloride was substituted for ether as the extraction solvent to eliminate flammability and peroxide problems. A sonication extraction procedure that has previously been successful for solid waste extraction replaced the Method 8150 hand extraction technique.

Ruggedness testing was employed to locate the key protocol experimental variables. Youden's experimental design was used to test seven experimental variables, at two levels each, in three basic experiments. These experimental designs are listed in Table 1. The three key extraction variables were the volume and pH of the buffer and the sonication power setting. The ester hydrolysis was sensitive only to the volume of added methanol. Ruggedness testing indicated that the optimized method would have a percent relative standard deviation (% RSD) of 11 or less.

Although ruggedness testing identifies sensitive method variables, it does not adjust these variables to their optimum value. The simplex optimization technique was selected to locate the best value for each of the experimental variables previously identified by ruggedness testing. The simplex technique is rapid and the experimental data generated can easily be computed by hand calculator. The simplex derived herbicide ester recoveries are listed in Table 2. The simplex results led to the preparation of a new analytical protocol.

The GC/EC linear dynamic quantification range and detection limit were determined. These values are listed in Table 2. The detection limits are higher, and the quantification range is narrower for MCPA and MCPP. Both of these conditions result from a GC/EC detector response which is weaker than that obtained for the other herbicide esters. This weaker response leads to GC column overloading at the high end of the linear dynamic range.

The effect of analyte level on extraction recovery was tested by spiking a herbicide still bottom sample and a kaolin clay, at various levels, with the herbicide methyl esters. Workup and subsequent analysis using the optimized protocol clearly indicated increased recoveries at higher analyte levels.

A GC/MS method was developed to confirm GC/EC tentative identifications. The minimum quantity of herbicide ester required to yield a Finnigan INCOS GC/MS computer search value of 800 (as recommended by the manufacturer's manual) under full scan conditions was determined. These values ranged from 0.3 to 4.5 nanograms.

Table 1. *Ruggedness Testing of Free Acid Herbicide Extraction and Analysis*

	Experimental Variables		
Condition No.	*Experiment No. 1*	*Experiment No. 2*	*Experiment No. 3*
1.	*pH of phosphate buffer added to clay*	*Volume of buffer or water added to clay*	*pH of phosphate buffer added to clay*
2.	*Acetone: hexane ratio in sonication*	*pH of buffer or water added to clay*	*Volume of buffer added to clay*
3.	*Analyte concentration*	*Sonicator output setting*	*Extraction solvent*
4.	*Size of breaker used for sonication*	*Sonication temperature*	*Sonicator output setting*
5.	*Base extraction or acid wash of clay extract*	*Solvent volume in sonication*	*Base extraction or acid wash of clay extract*
6.	*Clay extraction filter*	*Base extraction or acid wash of clay extract*	*Methylation solution*
7.	*Methylation solution*	*Amount of CH_2N_2 (molar excess)*	*Destruction of excess CH_2N_2*

Table 2. *Linear Dynamic Range, Detection Limit, and Percent Recoveries for Herbicide Methyl Esters*

Common Name	Systematic Name	Linear Range (ng/mL)	Detection Limit (ng/mL)*	% Recovery
2,4-D	2,4-dichlorophenoxy acetic acid	6.1 - 12200	1.7	91.2
2,4-DB	4-(2,4-dichlorophenoxy) butyric acid	20.2 - 40300	20.2	107.0
Dalapon	2,2-dichloropropanoic acid	7.4 - 736	1.34	-
Dicamba	3,6-dichloro-2-methoxy benzoic acid	2.6 - 520	0.6	85.4
Dichlorprop	2-(2,4-dichlorophenoxy) propionic acid	7.5 - 15000	1.9	95.2
Dinoseb	2-sec-butyl-4, 6-dinitro phenol	4.1 - 8100	1.4	89.6
MCPA	2-methyl-4-chlorophenoxy acetic acid	3.1 - 306	218.	96.1
MCPP, (Mecoprop)	2-(4-chloro-2-methyl-phenoxy) propionic acid	3.1 - 309	333.	101.0
Silvex	2-(2,4,5-trichlorophenoxy)-propionic acid	2.1 - 4140	0.53	85.7
2,4,5-T	(2,4,5-trichlorophenoxy) acetic acid	2.1 - 4110	0.78	80.9

**Quantity of herbicide methyl ester yielding a GC/EC detector response with S/N ≥ 3.*

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The complete report, entitled "Single-Laboratory Validation of EPA Method 8150 for the Analysis of Chlorinated Herbicides in Hazardous Waste," (Order No. PB 86-108 404/AS; Cost: $16.95, subject to change) will be available only from:

National Technical Information Service
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