



Project Summary

Single Laboratory Validation of EPA Method 8140

L. D. Betowski and P. J. Marsden

Method 8140, Organophosphorous Pesticides Parameters, of SW-846 was validated for use in the determination of 27 analytes in a single laboratory study. The method can be used for the analysis of 26 organophosphorous parameters in water, soil, and hazardous waste; the method is not suitable for monocrotophos because it showed poor recovery from soil and water. The performance of several GC columns, both packed and capillary, was established for the analysis of organophosphates. The use of megabore capillary GC columns over the use of packed columns specified in the current method is recommended for multiresidue organophosphorous analysis. Two phosphorus specific detectors, the flame photometric (FPD) and nitrogen phosphorus (NPD), were compared in terms of linearity, specificity, and sensitivity. Sample preparation and analysis techniques for organophosphates in aqueous and solid matrices were tested for ruggedness in order to identify critical method parameters. A proposed modification of Method 8140 is included together with accuracy and precision data for the determination of 26 method analytes in soil and water samples. Limited recovery data is also provided for additional organophosphorous compounds amenable to the method.

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

Method 8140, published in SW-846, Second Edition, is reported applicable to the analysis of 20 organophosphorous pesticides with detection limits in the range of 0.1 to 5 $\mu\text{g/L}$ for water. The method is a straightforward procedure in which samples are extracted with organic solvent, are concentrated, and are analyzed by GC with a phosphorus specific detector. Water samples are extracted by the use of one of two alternate procedures, Method 3510 (separatory funnel extraction) or Method 3520 (continuous liquid-liquid extraction). Two alternate preparation techniques are specified for soil samples and nonaqueous hazardous waste samples, Method 3540 (Soxhlet extraction) and Method 3550 (extraction by sonication). The gas chromatographic separation of the organophosphates is accomplished by using three packed columns, 5 percent SP-2401 on Supelcoport, 3 percent SP-2401 on Supelcoport, or 10 percent SE-54 on Gas Chrom Q (Teflon column). Two alternate phosphorus specific GC detectors are recommended: the nitrogen phosphorus (NPD) or flame photometric (FPD).

This report includes (1) a comparison of the recovery of 27 potential method analytes by using the sample preparation techniques specified for water and soil, (2) an evaluation of several packed and capillary columns with retention times for organophosphates of regulatory interest, and (3) a comparison of linearity, sensitivity, and detection limits of NPD and FPD detectors. A study of the applicability of cartridge cleanup techniques for analytes of Method 8140 is also

presented. Results of three ruggedness tests applied to sample preparation and analysis techniques are included with critical method criteria. Method bias and precision were established by conducting recovery studies of method parameters spiked at multiple concentration into each sample matrix.

Experimental Procedures

Method 8140 presently specifies the use of gas chromatography (GC) with single phase packed columns for the separation and quantitative determination of organophosphorous compounds. In this study, the evaluation of four packed GC columns was conducted: (1) 5 percent SP-2401; (2) 6 percent OV-210/4 percent SP-2100; (3) 10 percent DEGS; and (4) 10 percent SP-2330. All columns were 180 cm x 2 mm ID, with 100/120-mesh Supelcoport used as packing support. Both the FPD and NPD were used as detectors for the organophosphorous pesticides.

In addition to the evaluation of the above packed columns, the use of 30-m megabore capillary columns for the analysis of the organophosphorous pesticides was evaluated; the SPB-608 and the DB-210 columns were recommended in the modified Method 8140. The retention times and temperature programs for Method 8140 analytes on these two columns are shown in Table 1.

Method 8140 was evaluated for spiked water extracted by using Method 3510 (separatory funnel shakeout) or Method 3520 (continuous extractor) and for soil and solid wastes extracted by using Methods 3540 (Soxhlet extraction) or 3550 (sonication).

Ruggedness testing of Method 8140 was applied to the extraction of both water samples and soil samples. Seven variables were changed for the testing of the water samples. For the water samples, two conditions were tested for each of the following variables: duration of extraction, amount of sample, storage of extracts prior to analysis, amount of extraction solvent, concentration method, injection volume, and quantification method. For the soil samples, two conditions were tested for the following variables: sonication power, percent moisture of soil, extraction solvent, length of sonication, post-extraction filtration method, final concentration step, and use of GPC cleanup. In addition, a second ruggedness testing on soil was used in which the following variables were changed: type of extraction, percent moisture, spike level, filtration of extract

through sodium sulfate, concentration method, length of storage of unconcentrated extract, and use of GPC cleanup.

Table 1. Capillary Column Retention Times For Method 8140 Analytes

Compound	Capillary Column	
	SPB608	DB210
<i>Azinphos methyl</i>	38.04	37.24
<i>Bolstar</i>	35.08	37.55
<i>Chlorpyrifos</i>	26.88	25.18
<i>Coumaphos</i>	38.87	39.47
<i>Demeton, O,S</i>	15.90	17.24
<i>Diazinon</i>	20.02	19.68
<i>Dichlorous</i>	7.91	12.79
<i>Dimethoate</i>	20.18	27.96
<i>Disulfoton</i>	19.96	20.66
<i>EPN</i>	36.71	36.74
<i>Ethoprop</i>	16.48	18.67
<i>Fensulfthion</i>	35.20	36.80
<i>Fenthion</i>	29.45	28.86
<i>Malathion</i>	28.78	32.58
<i>Merphos</i>	21.73	32.44
<i>Mevinphos</i>	12.88	18.44
<i>Monocrotophos</i>	20.11	31.42
<i>Naled</i>	17.40	19.35
<i>Parathion, ethyl</i>	27.62	33.39
<i>Parathion, methyl</i>	23.71	32.17
<i>Phorate</i>	17.52	18.19
<i>Ronnel</i>	22.98	23.19
<i>Sulfotep</i>	18.02	19.58
<i>TEPP</i>	5.12	10.66
<i>Tetrachlorvinphos</i>	32.99	33.68
<i>Tokuthion</i>	24.58	39.94
<i>Trichloronate</i>	28.41	29.95

Temperature Program used for Both Capillary Columns:

<i>Initial temperature</i>	50°C
<i>Initial time</i>	1 minute
<i>Rate</i>	5°C/minute
<i>Final temperature</i>	140°C
<i>Hold 1</i>	10 minutes
<i>Rate</i>	10°C/minute
<i>Final temperature</i>	240°C
<i>Hold 2</i>	10 minutes

Results and Discussion

The single laboratory evaluation of Method 8140 has resulted in a modification of the method. This modified method which proposes the use of megabore capillary columns is presented as an appendix to the Project Report.

The linearity range and response factor for 27 Method 8140 analytes with a NPD are presented in Table 2. Similar data with an FPD are given in Table 3.

Two critical method variables for the extraction of soil were identified by ruggedness testing. Extraction with 1:1 methylene chloride/acetone (v/v) resulted in improved recoveries over methylene

chloride alone. The recoveries of organophosphorous pesticides were poorer following GPC cleanup versus no GPC. In a second ruggedness test on the soil, the spike level appeared to affect analyte recovery significantly. A 10-fold increase in spiking concentration resulted in a significant improvement in sample recovery. No critical method variables were identified in the ruggedness test for water samples. The overall standard deviation calculated from the ruggedness testing for water was 5.2 percent.

The recoveries were 50 to 80 percent for most spiked organophosphorous compounds when use was made of the Soxhlet extractor, while only 40 to 70 percent were recovered for these same analytes by using sonication. The relative standard deviation for the method under either Soxhlet extraction or sonication for most analytes is roughly equivalent (5 to 15 percent).

Although the extraction procedure was not identified as a critical method variable, analyte recoveries from water at low and medium concentrations were generally lower for continuous liquid extraction (Method 3520) versus separatory funnel (Method 3510) extraction. This may have been due to hydrolysis of analyte in the longer continuous extraction process. It is important to remember that this difference was observed in the extraction of clean water. For some environmental samples, the loss of analytes in emulsions formed in the separatory funnel could make continuous liquid extraction the preferred method.

Conclusion and Recommendations

The present Method 8140 is a packed column technique suitable for the analysis of twenty compounds. Because there were shortcomings in this method in the area of GC resolution when it was applied to a longer list of analytes, a modified method has been proposed. The modified Method 8140 of SW-846 was applied to the determination of 27 organophosphorous analytes in water and soil. This method has been validated for use with 26 of these compounds. The method cannot be used for monocrotophos since recoveries of no greater than 20 percent were achieved for this compound. This new version of Method 8140 allows the use of megabore capillary columns: a polar column (DB-210 or equivalent) is recommended as the primary column and a moderate polarity column (SP-608

or equivalent) is proposed for the secondary column. The modified method represents an improvement over the older technique and can be used to generate data of good quality with excellent repeatability.

The modified Method 8140 requires that aqueous samples be extracted with methylene chloride, and that solids be extracted with a 1:1 methylene chloride/acetone (v/v) solvent mixture. A caution has been added that the analyst should use a drying agent only if necessary, since single laboratory results indicate that some organophosphorous analytes are lost during drying with sodium sulfate. The laboratory is allowed to use either Kuderna-Danish (K-D) or rotary evaporation to reduce the volume of sample extracts. Analysts are cautioned that samples should not be transferred with 100 percent hexane during sample workup as the more water soluble organophosphorous compounds may be lost. No sample cleanup is required for Method 8140 nor was one validated for its use.

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-03-1958 to S-CUBED, a Division of Maxwell Laboratories, Inc., San Diego, California. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

Table 2. Response Factors For 27 Method 8140 Analytes on a Nitrogen-Phosphorus Detector

Compound	Range (ng)	Response Factor (Response/ng)
Azinphos methyl	5-500	2.46×10^4
Bolstar	0.545-545	6.85×10^3
Chlorpyrifos	5.2-520	6.27×10^4
Coumaphos	1.05-525	2.34×10^4
Demeton	13.7-274	1.10×10^4
Diazinon	5.8-580	1.68×10^4
Dichlorvos	4.76-4760	2.05×10^4
Dimethoate	1.07-107	2.29×10^4
Disulfoton	0.720-144	5.42×10^5
EPN	0.62-620	1.61×10^4
Ethoprop	0.61-610	3.81×10^4
Fensulfthion	6.9-575	3.88×10^4
Fenthion	7.45-745	5.15×10^4
Malathion	1.2-600	3.64×10^4
Merphos	42.6-4260	4.48×10^3
Mevinphos	7.05-705	2.09×10^4
Monocrotophos	42.6-4260	2.59×10^3
Naled	—	ND
Parathion, ethyl	1.35-675	3.70×10^4
Parathion, methyl	1.28-640	2.74×10^4
Phorate	1.39-139	1.94×10^4
Ronnel	0.525-210	3.97×10^5
Sulfotep	6.67-266	6.78×10^4
TEPP	6.52-6520	3.71×10^3
Tetrachlorvinphos	1.03-515	1.67×10^3
Tokuthion	1.39-695	2.21×10^4
Trichloronate	—	ND

ND = Not determined.

Table 3. Response Factors For 27 Method 8140 Analytes on a Flame Photometric Detector

Compound	Range (ng)	Response Factor (Response/ng)
Azinphos methyl	5-500	2.28×10^4
Bolstar	0.545-218	5.12×10^4
Chlorpyrifos	0.52-520	6.27×10^4
Coumaphos	0.525-525	2.49×10^4
Demeton	—	ND
Diazinon	1.16-232	8.56×10^4
Dichlorvos	4.76-4760	3.08×10^3
Dimethoate	0.535-535	2.77×10^4
Disulfoton	0.720-720	2.79×10^4
EPN	0.62-248	4.38×10^4
Ethoprop	0.61-610	3.29×10^4
Fensulfthion	0.690-690	1.86×10^4
Fenthion	0.745-745	2.95×10^4
Malathion	0.60-600	2.95×10^4
Merphos	8.51-1700	2.48×10^4
Mevinphos	14.1-705	2.38×10^4
Monocrotophos	8.57-1700	2.47×10^3
Naled	10-500	1.46×10^3
Parathion, ethyl	0.675-675	3.53×10^4
Parathion, methyl	0.640-640	2.76×10^4
Phorate	1.39-278	3.04×10^4
Ronnel	0.525-525	3.35×10^4
Sulfotep	0.665-266	6.97×10^4
TEPP	13.0-6520	2.90×10^2
Tetrachlorvinphos	0.515-515	3.11×10^4
Tokuthion	0.695-695	1.96×10^4
Trichloronate	0.5-100	2.98×10^4

ND = Not determined.

*Paul J. Marsden is with Maxwell Laboratories, Inc., La Jolla, CA 92038-1620;
the EPA author **Leon D. Betowski** is with the Environmental Monitoring
Systems Laboratory, Las Vegas, NV 89114.*

***Llewellyn Williams** is the EPA Project Officer (see below).*

*The complete report, entitled "Single Laboratory Validation of EPA Method
8140," (Order No. PB 87-177 507/AS; Cost: \$18.95, subject to change) will
be available only from:*

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
P.O. Box 15027
Las Vegas, NV 89114*

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use \$300

EPA/600/S4-87/009.

0000329 PS
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604

