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Feasibility Research on Alternative Approaches for Sampling and Extraction Methods in the TO-4A Method for Pesticides in Ambient Air with Analysis by GC/MS and LC/MS/MS

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Abstract

This compilation of methods is the result of a Regional Methods project between the U.S. Environmental Protection Agency (EPA) Region 4 and the EPA's Office of Research and Development. The research leading to these methods was conducted in response to a need to update an EPA compendium method to use the best currently available technology and incorporate green chemistry concepts. The purpose of this research was to evaluate the feasibility of a new procedure for sampling and analysis of pesticides in ambient air.

This work assessed alternatives for the collection, extraction, and analytical methods described in compendium method TO-4A "Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam Sampling Followed by Gas Chromatographic/Multi-Detector Detection."[1] The TO-4A method uses polyurethane foam (PUF) sampling media and requires separate assemblies for sampling, shipping, and extraction. The analytes are stripped from the PUF in Soxhlet extractors. The resulting extract is reduced in volume and then cleaned with alumina or silica. Analysis is by gas and liquid chromatography with one of several relatively nonspecific detectors.

The methods described here use integrated devices and automated processes for the determination of the pesticides listed in TO-4A, thereby simplifying it and reducing solvent requirements and the need to handle the sampling media. A modified, reusable, stainless steel accelerated solvent extraction cell, packed with a pre-cleaned resin, functions as the sampling device, shipping container, and extraction vessel. Finally, mass spectrometers replace the electron capture, flame photometric, nitrogen-phosphorus, and ultraviolet absorption detector listed in method TO-4A.

To evaluate the effectiveness of the overall process, the work was divided into component methods that could be optimized individually. Standard operating procedures (SOPs) were written for each of the final procedures. Although these SOPs are somewhat specific to this particular EPA research situation, they can be used as a starting point for further development outside their original intended use. The components of the method are (1) media and sampler preparation, (2) sample collection, (3) extraction, (4) cleanup, and (5) analysis. The accuracy and precision of the finalized procedures were assessed separately and as a whole method.

Analytical sensitivity for these pesticides matched or exceeded that achieved using the detectors listed in the TO-4A method. The proposed method was found to have some limitations compared to the TO-4A. The highest achievable air flow rates through the XAD-2 sorbent cartridge were less than those possible with TO-4A. Of the 54 pesticides listed in the method, 48 could be analyzed using the current generation analytical instruments. Difficulties in precision also were encountered; in many instances the relative standard deviations of recoveries from replicate trials was higher than 20%. The marginal loss in sensitivity and precision are offset by gains in specificity, efficiency, and potential reductions in solvent use.

Executive Summary

Background
Compendium method TO-4 was first published as a U.S. Environmental Protection Agency (EPA) report in 1984. The report was one of a series of air toxic methods in "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air," (EPA 600/4-89-018). In 1999, TO-4 was updated to incorporate current technologies, and the revision was published as method TO-4A, "Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)," in the second edition of the compendium.[1]

Briefly, TO-4A describes procedures to sample ambient air and determine concentrations of selected common pesticides and polychlorinated biphenyls (PCBs). Air sampling is via a high-volume pump with polyurethane foam in a glass cartridge as the collection media. The analytes are extracted from the PUF in Soxhlet extractors, and the resulting sample is cleaned up using alumina or silica. Analysis is by GC in conjunction with one of several detectors or by high-performance liquid chromatography (HPLC) with a UV or electrochemical detector.

In 2002, a collaborative Regional Methods project was proposed by scientists in Region 4 to work with the Office of Research and Development in evaluating alternative methods of sampling and analysis for possible inclusion in TO-4A. The project, "Demonstration and regional field testing of sampling and analytical method for sampling pesticides and semi-volatile organic compounds using an adsorbent resin sampling system, accelerated solvent extraction, and GC/MS analysis," proposed replacing the sampling and extraction procedures in TO-4A with methods using an integrated system. Ultimately, the project was expanded to replace the electron capture, flame photometric, and nitrogen-phosphorus detectors (ECD, FPD, and NPD, respectively) and the ultraviolet absorption (UV) and fluorescence (Flor) detector listed in method TO-4A with current-generation single and tandem mass spectrometers (MS, MS/MS).

Objectives
This work provides alternatives to the sampling, extraction, and analysis methods described in EPA compendium method TO-4A. Currently, the compendium methods require a PUF sampling media and separate assemblies for sampling, shipping, and extraction. The proposed methods use integrated devices and automated procedures for the determination of these compounds, thereby simplifying the methods and reducing the need to handle the media. The method uses accelerated solvent extraction (ASE) cells packed with XAD-2 resin to function both as a sampling device and an extraction vessel. Since the same durable vessel is used for sampling and extraction, the following benefits are expected:

- less analyte lost during sample transport and processing,
- fewer samples lost due to glass breakage,
- reduction in use of organic solvents for rinsing, and
- simplification of sampling and extraction procedures.

Organization
This compilation of methods (Appendices A through G) contains seven SOPs that detail the steps of the final approach: (1) media preparation, (2) sampler preparation, (3) air sampling, (4) sample extraction, (5) sample cleanup, (6) GC/MS analysis, and (7) LC/MS/MS analysis. It is important to note that these SOPs are specific to the work conducted for this study. They provide an excellent starting place for modification, enabling more general use.

Approach
The SOPs presented here are to be used in conjunction with those for more general laboratory procedures, such as the preparation of standards and balances. Local procedures for laboratory operations, health and safety, and waste disposal must be considered and followed.

Media Preparation
Amberlite XAD-2 resin was selected as a sorbent material. The resin was cleaned using a solvent series (in order of decreasing polarity), and cleanliness was verified using ECD. Instructions for cleaning of XAD-2 prior to reuse are included in the SOP in Appendix A.

Sampling Device
The ASE cells purchased from the manufacturer were modified with two sets of grooves to allow for a snap ring and mesh screen to hold 4 in of XAD between them. A fabricated adapter enabled connection of a 100-mL stainless steel ASE cell to a high-vacuum pump with flow controller. Setup of this device is described in the SOP in Appendix B.

Sample Collection
Gast vacuum pumps were turned on and run for 16 to 24 h at a predetermined flow rate. Once the sampling period was complete, the cells were unscrewed from the sampler, recapped, and placed directly on the extraction device for automated extraction. This procedure is detailed in the SOP in Appendix C.

Sample Extraction
An automated ASE was used for sample extraction, as outlined in the SOP in Appendix D. Surrogate solutions were added through the screen onto the sorbent material. The samples were extracted using 20% acetone in hexane heated to 75 °C at 1500 psi. The cell can be reused for further air sampling without disassembly or replacement of the sorbent material.

Sample Cleanup
Samples were concentrated using solvent evaporation, then loaded onto a Florisil (10 g) column. The column was then eluted with progressively more polar combinations of ethyl acetate (EtOAc) in hexane, which were split for analysis using GC and LC. This procedure is explained in the SOP in Appendix E. Additional solvent and time savings could be realized using a similar procedure adapted to solid-phase extraction cartridges.

Sample Analysis by GC/MS
Appendix F contains the SOP for GC/MS analysis of 36 pesticides as identified in compendium method TO-4A. Three internal standards and four surrogate standards are added for quality assurance and quality control (QA/QC) purposes. Optimal GC/MS settings are described along with retention times and fragmentation patterns for each compound.

Sample Analysis by LC/MS/MS
Appendix G contains the SOP for LC/MS/MS analysis of 23 pesticides as identified in compendium method TO-4A. Four internal standards and four surrogate standards are added for QA/QC purposes. Optimal LC/MS/MS settings are described along with retention times and product ions for each compound.

Conclusions
The SOPs that follow provide the details of the final methods produced from this research. This research demonstrated that it is feasible to replace the current sampling assembly described in method TO-4A with an alternative that uses a modified stainless steel ASE cell to function both as the sampling device and the extraction vessel. XAD resin, used as the collection media, appeared effective in trapping most of the pesticides for which it was tested. However, the highest achievable air flow rates through the XAD were less than used by TO-4A. Automated ASE provided acceptable recoveries of the majority of the analytes and reduced solvent and time requirements compared to Soxhlet extraction. Additionally, same cell use for sampling and extraction proved very efficient for sample processing and recordkeeping by eliminating the transfer between multiple vessels.

1.0 Introduction

1.1 Background

Pesticide usage and environmental distribution are common to rural and urban areas of the United States. The application of pesticides can cause adverse health effects in humans by contaminating soil, water, air, plants, and animal life. Polychlorinated biphenyls (PCBs) are less widely used because of extensive restrictions, but still cause problems due to their presence in various electrical products. Many pesticides and PCBs exhibit bioaccumulative, chronic health effects; therefore, monitoring the presence of these compounds in ambient air is of great importance.[2,3]

The relatively low levels of such compounds in the environment require the use of high-volume sampling techniques to acquire sufficient samples for analysis. However, the volatility of these compounds prevents efficient collection on filter media. Consequently, compendium method TO-4A utilizes both a particle filter and a polyurethane foam backup cartridge that provides for efficient collection of most common pesticides, PCBs, and other organics within the same volatility range. Moreover, modifications to this method have been applied successfully to measurement of common pesticides and PCBs in outdoor and indoor air and for personal respiratory exposure monitoring.

The TO-4A method covers sampling and analysis of a variety of common pesticides and PCBs in ambient air (Table E2. Solvent type and volume for six Florisil column eluants). The procedure is based on the adsorption of chemicals from ambient air on PUF using a high-volume sampler. The high-volume PUF sampling procedure is applicable to multicomponent atmospheres containing common pesticide concentrations from 0.001 to 50 µg/m^3 over 4- to 24-h sampling periods. The limits of detection will depend on the nature of the analyte and the length of the sampling period. The analytical methodology described in compendium method TO-4A is currently employed by laboratories throughout the United States and typically uses GC and/or HPLC.

Table 1-1. TO-4A target analyte list with suggested analysis method[1]

Compound	Recommended analysis[a]	Compound	Recommended analysis[a]
Alachlor	GC/ECD	Folpet	GC/ECD
Aldrin	GC/ECD	Heptachlor	GC/ECD
Allethrin	HPLC/UV	Heptachlor epoxide	GC/ECD
Aroclor 1242	GC/ECD	Hexachlorobenzene	GC/ECD
Aroclor 1254	GC/ECD	Lindane (g-BHC)	GC/ECD
Aroclor 1260	GC/ECD	Linuron	HPLC/UV
Atrazine	GC/NPD	Malathion	GC/NPD or FPD
Bendiocarb	HPLC/UV	Methyl parathion	GC/NPD or FPD
BHC (a- and b-hexachlorocyclohexanes)	GC/ECD	Methoxychlor	GC/FCD
Captan	GC/ECD	Metolachlor	GC/ECD
Carbaryl	HPLC/UV	Mexacarbate	GC/FCD
Carbofuran	HPLC/UV	Mirex	GC/ECD
Chlordane, technical	GC/ECD	Monuron	HPLC/UV
Chlorothalonil	GC/ECD	Trans-nonachlor	GC/ECD
Chlorotoluron	HPLC/UV	Oxychlordane	GC/ECD
Chlorpyrifos	GC/ECD	Pentachlorobenzene	GC/ECD
2,4-D esters and salts	GC/ECD	Pentachlophenol	GC/ECD
Dacthal	GC/ECD	Permethrin (cis- and trans-)	HPLC/UV
p,p′-DDT	GC/ECD	o-Phenylphenol	HPLC/UV
p,p′-DDE	GC/ECD	Phorate	GC/NPD or FPD
Diazinon	GC/NPD or FPD	Propazine	GC/NPD
Dicloran	GC/ECD	Propoxur (Baygon)	HPLC/UV

Compound	Recommended analysis[a]	Compound	Recommended analysis[a]
Dieldrin	GC/ECD	Pyrethrin	HPLC/UV
Dicofol	GC/ECD	Resmethrin	HPLC/UV
Dicrotophos	HPLC/UV	Ronnel	GC/ECD
Diuron	HPLC/UV	Simazine	HPLC/UV
Ethyl parathion	GC/NPD or FPD	Terbuthiuron	HPLC/UV
Fenvalerate	HPLC/UV	Trifluralin	GC/ECD
Fluometuron	HPLC/UV		

[a]GC = gas chromatography, ECD = electron capture detector, FPD = flame photometric detector, HPLC = high-performance liquid chromatography, NPD = nitrogen-phosphorus detector, UV = ultraviolet absorption detector

1.2 Strengths and Weaknesses of TO-4A

The strengths of the TO-4A method are that it can detect environmentally relevant concentrations of a variety of pollutants and current-use pesticides. It has been registered with ASTM International and is used by many scientists with readily accessible analytical techniques.

The weaknesses of the TO-4A method are that it uses a fragile glass sampler cartridge and large, noisy pumps for sample collection. Sample cartridges are comprised of two different sorbent materials, which must be transferred prior to extraction. Air must be collected for a 24-h period to accumulate detectable levels of target analytes. Large quantities of solvent and time are required for thorough extraction of all analytes and several GC detectors are required for adequate detection of all analytes.

1.3 What was Needed to Improve TO-4A and Goals for this Project

The SOPs presented here proposes methods to replace TO-4A with newer technology. The overall goals are to address the weaknesses listed above, and specifically to

- reduce the size and noise level of the sampler;
- find a sturdier material, such as stainless steel, to replace the glass sampling cartridge;
- replace methylene chloride with a less toxic solvent;
- reduce the extraction time per sample;
- reduce the volume of solvent required to process a sample; and
- match or improve the measurement quality objectives for
    - sensitivity,
    - selectivity,
    - analyte recovery,
    - reproducibility,
    - accuracy, and
    - precision.

2.0 Methods

The final procedures used for each process in this report are detailed in Appendices A through G.

2.1 Media Preparation

The SOP for media preparation (XAD-2 cleaning procedure, Using the Dionex Accelerated Solvent Extractor 300) is provided in Appendix A. XAD-2 resin was selected as the sorbent of choice for this project. XAD is often used in environmental sampling for air and water and is sometimes used in a sandwich fashion (between PUF plugs) for the TO-4A and ASTM 4861 methods. XAD was selected for prior performance with these compounds, stability, availability of "clean" materials, and adsorption characteristics.

Prior to air sampling, 100-mL accelerated solvent extraction (ASE) cells were packed with XAD-2 resin and precleaned on a Dionex 300 using sequential extractions with methanol, acetone, dichloromethane, hexane, and 20% acetone in hexane. The 20% acetone in hexane extracts were checked for a clean background before further use. To insure that all compounds from previous experiments were removed, reused XAD cartridges were extracted with acetone and checked for a clean background.

2.2 Sampler Preparation

The SOP for preparation and packing ASE cells (Preparation and Packing of ASE Cells for Air Sampling with XAD-2) is provided in Appendix B. The TO-4A method requires a high-volume sampler capable of pulling ambient air through the filter/adsorbent cartridge at a flow rate of ~0.225 m^3/min to obtain a total sample volume of greater than 300 m^3 over a 24-h period. To meet research objectives, a Gast vacuum pump (model 0523-101Q-SG588DX) was selected in conjunction with a Teledyne Hastings Instruments flow controller (model THPS-100). This flow controller is capable of setting the flow from 0 to 0.1 m^3/min, with a maximum sample of ~150 m^3 over a 24-h period. An adapter was fabricated to enable a stainless steel, 100-mL ASE cell to be directly attached to the unit.

The glass sampling cartridge in the TO4A method was replaced with a modified 100-mL stainless steel ASE cell. The ASE cells were modified so that they could be unscrewed from the sampler, recapped, and placed directly on the ASE for automated extraction. The ASE cells were also modified by etching two sets of grooves to allow for a snap ring and mesh screen to hold 4 in of XAD between them.

2.3 Air Sampling

The SOP for air sampling using ASE cells (Air Sampling with ASE Cells) is provided in Appendix C. Prior to air sampling, the XAD in each cell was spiked with 1 mL of the target analytes in ethyl acetate (EtOAc; 400 ng/mL) or 1 mL of EtOAc only (blanks). The cells were attached to the pumps, and the flow rates were set to either zero flow or 30 L/min. Ambient air was pulled through the pumps for 19, 24, or 48 h.

2.4 Sample Extraction

The SOP for sample extraction from XAD in ASE cells (Extracting TO-4A Air Samples with the Dionex ASE 300) is provided in Appendix D. The ASE 300 was used for all extraction experiments. Using spiked XAD in ASE cells, the extraction efficiency of three solvent systems (hexane, 10% acetone in hexane, and 20% acetone in hexane) was compared. Overall, 20% acetone in hexane gave the best recovery, and recovery for the TO-4A compounds that were tested ranged from 66% to 112%.

2.5 Sample Cleanup

The SOP for sample cleanup of TO-4A pesticides extracted from XAD (Florisil Column Cleanup for TO-4A Pesticides in Air Samples) is provided in Appendix E. Four cleanup procedures were evaluated. Three used Florisil (1 or 10 g), and one used silica (0.5 g). Elutropic solvent combinations, including hexane, toluene, and EtOAc, were evaluated. In each case, the compounds were loaded onto the cleanup column or cartridge in hexane. The procedure giving the most effective cleanup and recovery was

- 1 mm ID column with Florisil (10 g),
- 125 mL 6% EtOAc in hexane,
- 125 mL 15% EtOAc in hexane,
- 125 mL 50% EtOAc in hexane, and
- 125 mL 100% EtOAc.

This procedure was run in triplicate and gave an average recovery of 86% (all trials and compounds combined) and was the cleanup procedure used for sample analysis.

2.6 Sample Analysis Using GC/MS

GC/MS was used to analyze the relevant pesticides as identified in Compendium Method TO-4A. The SOP for GC/MS analysis of TO-4A pesticides is provided in Appendix F. Surrogate and internal standards were added as a part of the QC, with the surrogates added to the XAD prior to extraction, and the internal standards added to the sample extract just before injection. The pesticides analyzed via GC/MS and their surrogate and internal standards are provided in Table 2-1. GC/MS target analytes, surrogates, and internal standards 2-1.

Table 2-1. GC/MS target analytes, surrogates, and internal standards

GC target analytes			
Alachlor[b]	Aldrin[b]	Atrazine[a]	Captan[c]
cis-Chlordane[c]	*trans*-Chlordane[c]	Chlorothalonil[b]	Chlorpyrifos[b]
2,4-D ethyl ester[a]	2,4-D methyl ester[a]	Dacthol[b]	*p,p'*-DDE[c]
o,p'-DDT[c]	*p,p'*-DDT[c]	Diazinon[b]	Dicloran (Botran)[a]
Dieldrin[c]	Ethyl parathion[b]	Fenchlorphos (Ronnel)[b]	Folpet[c]
a-HCH[a]	b-HCH[a]	Heptachlor[b]	Heptachlor epoxide B[c]
Hexachlorobenzene[a]	Lindane (g-HCH)[b]	Malathion[b]	Methyl parathion[b]
Methoxychlor[c]	Metolachlor[b]	Mirex[c]	*trans*-Nonachlor[c]
Oxychlordane[c]	Propazine[a]	Simazine[a]	Trifluralin[a]
GC surrogate standard compounds			
$^{13}C_3$ Atrazine[a]	D_{10} Chlorpyrifos[b]	D_{10} Diazinon[b]	Heptachlor epoxide A[c]
GC internal standard compounds			
TCmX	13C6 d-HCH	DCBP	

[a]Target analytes and surrogates using TCmX as an internal standard
[b]Target analytes and surrogates using $^{13}C_6$ d-HCH as an internal standard
[c]Target analytes and surrogates using DCBP as an internal standard

2.7 Sample Analysis Using LC/MS/MS

LC/MS/MS was used to analyze the relevant "HPLC" pesticides as identified in Compendium Method TO-4A. The SOP for LC/MS/MS analysis of TO-4A pesticides is provided in Appendix G. The pesticides analyzed via LC/MS/MS and their surrogate and internal standards are provided in Table 2-1. GC/MS target analytes, surrogates, and internal standards2-2.

Table 2-2. LC/MS/MS target analytes and internal standards

LC target analytes			
Allethrin[d]	Atrazine[a]	Bendiocarb[a]	Carbaryl[a]
Carbofuran[a]	Chlortoluron[a]	Cinerin I[d] & II[b]	Diazinon[b]
Diuron[a]	Dicrotophos[a]	Fenvalerate[d]	Fluometuron[a]
Jasmolin I[d] & II[b]	Linuron[a]	Monuron[a]	*cis*-Permethrin[c]
trans-Permethrin[d]	Propazine[a]	Propoxur (Baygon)[a]	Pyrethrin I[d] &II[b]
Resmethrin[d]	Simazine[a]	Tebuthiuron[a]	
LC internal standard compounds			
$^{13}C_3$ Atrazine	D_{10} Diazinon	$^{13}C_6$ *cis*-permethrin	$^{13}C_6$ *trans*-permethrin

[a]Target analytes using $^{13}C_3$ Atrazine as an internal standard
[b]Target analytes using D_{10} Diazinon as an internal standard
[c]Target analytes using $^{13}C_6$ *cis*-Permethrin as an internal standard
[d]Target analytes using $13C_6$ *trans*-Permethrin as an internal standard

3.0
Results and Discussion

3.1 Compounds Removed

To simplify the evaluation of the new methods, the Aroclor PCB mixtures listed in TO-4A were excluded from the spiking mixture, and only the TO-4A pesticides were used. Several pesticides were removed from the analyte list during method development because the measurement quality objectives could not be met. Details are provided in Table 3 1.

Table 3-1. TO-4A analytes removed from consideration in new method

Compound	Reason for removal
Dicofol	Breakdown occurred in standards, poor chromatography
Mexacarbate	Poor sensitivity/recovery
Pentachlorobenzene	Inconsistent recovery/sensitivity
Pentachlorophenol	Did not elute from column/chromatography issues, <20% recovery
Phorate	Inconsistent and <35% recovery
o-Phenylphenol	Poor sensitivity
PCBs	Method evaluation restricted to pesticides

3.2 Research Quality Objectives, Limit of Detection (LOD)

The measurement quality objectives for LOD are detailed in Table 3 2. In all but two compound classes (organic compounds [OC's] and carbamates), the TO-4A LOD was matched or improved.

Table 3-2. Limit of detection (LOD)

		LOD (ng/mL)		
Compound class	Detector	TO-4A[a]	GC/MS[b]	LC/MS-MS[b]
OCs	ECD	1-50	50	50
OPs	FPD/NPD	50-500	50	50
Triazine, carbamate, urea	NPD/GC-MS	50-200	50	50
Triazine, carbamate, urea	HPLC-UV	1000-5000	50	50
Carbamates	HPLC-Flor	10-100	50	50
Carbamate, urea, pyrethroid, phenolic	HPLC-UV	200-10,000	50	50

[a]TO-4A LOD as listed in the compendium method[1]
[b]GC/MS and LC/MS-MS LOD is defined as the concentration of the least concentrated calibration standard.

Table 3-3. Time of attended and unattended operations for pesticide analysis

	TO-4A		New method	
Process	Attended (h)	Unattended (h)	Attended (h)	Unattended (h)
Matrix cleaning, initial	0.5	16[a]	0.5	1.5
Matrix cleaning, reuse	0.5	16	<0.1	0.25
Media prep[b]	0.5	—	<0.1	—
Sampler prep[c]	1.0	—	<0.1	0.5
Extraction	0.25	16	<0.1	0.25
Sample cleanup	0.5	—	6[d]	—
Total, initial	3.25	32	6.8	2.25
Total, reuse	3.25	32	6.4	1.0

[a]16 h is required for the PUF cleaning procedure; 5 h is required for baking the glass fiber filter, which can take place during the PUF cleaning procedure. Filters for the separate collection of particulates were not considered in the new method.

[b]Includes media preparation and cartridge assembly

[c]Includes flow calibration and flow controller warm-up times

[d]This procedure should be transferred to SPE cartridges, which require significantly less time (<1 h)

Two of the primary reasons for undertaking this method update were to decrease both the time of operations and volume of solvent required. Table 3 3 details the amount of time required for both the TO-4A and new methods. The same amount of time (35.25 h) is required for sample collection and cleanup with the TO-4A method, regardless of whether it is the initial or reuse of the sampling matrix. By reusing the matrix in the new method, about 1.5 h of processing is saved compared with using fresh matrix. The time for unattended operations is significantly less with the new method (2.25 h versus 32 h). The sample cleanup in the new method is the longest step, requiring 6 h. If this step is transferred to solid phase extraction (SPE) cartridges, it will take less than 1 h, making the new method shorter than the TO-4A method.

Table 3 4 details the volume of solvent required for taking one sample through the entire method. Dichloromethane was eliminated in all steps, except initial matrix cleaning. If the solvent needed to initially clean the XAD is included, the TO-4A method uses 1450 mL of solvent, whereas the new method uses 1720 mL. If the matrix already has been used, the TO-4A method uses the same 1450 mL of solvent, whereas the new method uses 970 mL, saving nearly 500 mL of solvent. It is important to note that the new method is using large quantities of solvent for the sample cleanup, which can be reduced significantly by transferring the cleanup method to SPE cartridges for an additional 600 mL solvent savings.

Table 3-4. Volume of solvent used for pesticide analysisw

Process	TO-4A	New method
Matrix cleaning, initial	700 mL	900 mL
Matrix cleaning, reuse	700 mL	150 mL
Extraction	700 mL	150 mL
Sample cleanup	50 mL	670 mL [a]
Total, initial	1450 mL	1720 mL
Total, reuse	1450 mL	970 mL

[a]This procedure could be transferred to SPE cartridges, which require significantly less solvent (<50 mL)

3.3 Data Quality Objectives, Recovery

Using the final preparation, extraction, and cleanup procedures, a series of trials using spiked XAD was performed to evaluate the complete method. Duplicate sampling trains were attached to pumps that were set to draw air through the XAD at the maximal rate possible (~50 m3 in 24 h). After turning on the pumps, the XAD was spiked through the retaining screen with the target analytes and, usually, the GC surrogate standards. Additionally, one control matrix spike was prepared for each trial for comparison. This sample was spiked with the target analytes but was not put on a sampler and no air was collected.

The average recovery and relative standard deviation (RSD) from method evaluation experiments are detailed in Table 3 5 for GC compounds and in Table 3 6 for LC compounds. For comparison, in method TO-4A, the RSDs range from 5% to 30%, and the acceptable recoveries range from 65% to 125%. The acceptable recovery range for the new methods is 75% to 120%, and the variability target is RSD <20%. The reproducibility is similar for the new GC method and higher for the new LC method. Typically, the new methods are in the acceptable range, but there have been instances of unreasonably low or high recovery for specific compounds, which remains unexplained. It is important to note that most compounds met the measurement quality objectives, but there is still room to improve both the accuracy and precision of the method.

Table 3-5. Comparative recoveries of spiked GC pesticides (percent recovery ± relative standard deviation)

Compound	No air flow (n = 7)	With air flow[a] (n = 11)
$^{13}C_3$ Atrazine (surrogate)	125 ± 32	120 ± 26
$^{13}C_6$ δ-HCH (surrogate)	99 ± 17	107 ± 6
2,4-D Ethyl Ester	60 ± 45	86 ± 32
2,4-D Methyl Ester	62 ± 53	103 ± 8
Alachlor	143 ± 17	157 ± 24
Aldrin	73 ± 33	93 ± 20
a-HCH	58 ± 45	89 ± 15
Atrazine (GC)	82 ± 17	95 ± 32
b-HCH	90 ± 11	195 ± 57
Captan	94 ± 43	108 ± 64
Chlorothalonil	134 ± 33	193 ± 38
Chlorpyrifos	75 ± 28	76 ± 50
cis-Chlordane	80 ± 10	101 ± 35
D_{10} Chlorpyrifos (surrogate)	62 ± 24	71 ± 40
D_{10} Diazonon (surrogate)	61 ± 30	72 ± 35
Dacthal	97 ± 12	108 ± 13
Diazinon (GC)	78 ± 36	74 ± 22
Dicloran (Botran)	105 ± 21	127 ± 25
Dieldrin	101 ± 28	120 ± 28
Ethyl Parathion	92 ± 22	85 ± 15
Fenchlorphos (Ronnel)	102 ± 17	96 ± 25
Folpet	126 ± 65	100 ± 22
g-HCH (Lindane)	77 ± 27	97 ± 25
Heptachlor	79 ± 29	67 ± 38
Heptachlor Epoxide A	78 ± 17	71 ± 11
Heptachlor Epoxide B	75 ± 17	92 ± 33
Hexachlorobenzene	36 ± 67	77 ± 24
Malathion	116 ± 22	128 ± 19
Methoxychlor	101 ± 7	143 ± 36
Methyl Parathion	94 ± 30	96 ± 13
Metolachlor	104 ± 11	119 ± 16
Mirex	96 ± 19	115 ± 41
o,p'-DDT	89 ± 7	118 ± 40
Oxychlordane	96 ± 17	117 ± 16
p,p'-DDE	99 ± 22	118 ± 38
p,p'-DDT	88[b]	176 ± 28
Propazine (GC)	99 ± 17	109 ± 24
Simazine (GC)	109 ± 26	130 ± 23
trans-Chlordane	79 ± 10	98 ± 36
trans-Nonachlor	103 ± 22	128 ± 16
Trifluralin	64 ± 45	87 ± 28

[a]Samples were attached to pumps that ran between 18 and 48 h.

[b]n = 1 for this compound, therefore no standard deviation is reported.

Table 3-6. Comparative recoveries of spiked LC pesticides (percent recovery ± relative standard deviation)

Compound	Without air flow (n = 8)	With air flow[a] (n = 16)
Allethrin	92 ± 22	84 ± 31
Atrazine	117 ± 24	108 ± 25
Bendiocarb	118 ± 41	94 ± 20
Carbaryl	100 ± 25	85 ± 20
Carbofuran	74 ± 42	64 ± 32
Chlorotoluron	98 ± 20[b]	74 ± 16[c]
Cinerin I	92 ± 19	90 ± 37
Cinerin II	84 ± 23	75 ± 30
Diazinon	131 ± 35	117 ± 36
Dicrotophos	63 ± 33[b]	56 ± 31[c]
Diuron	85 ± 24	74 ± 23
Esfenvalerate	96 ± 22	88 ± 23
Fluometuron	129 ± 16[b]	89 ± 27[c]
Jasmolin I	83 ± 24	73 ± 27
Jasmolin II	82 ± 23	71 ± 28
Linuron	96 ± 16	87 ± 13
Monuron	101 ± 19[b]	73 ± 15[c]
Cis- and *Trans*-Permethrin	94 ± 15	91 ± 28
Propazine	127 ± 25	117 ± 28
Propoxur (Baygon)	90 ± 38	87 ± 31
Pyrethrin I	72 ± 41	58 ± 45
Pyrethrin II	68 ± 47	54 ± 47
Resmethrin	67 ± 38	48 ± 55
Simazine	138 ± 32	120 ± 34
Tebuthiuron	108 ± 28[b]	87 ± 20[c]

[a]Samples were attached to pumps that ran between 18 and 48 h.
[b]n = 3
[c]n = 10`

Bibliography

[1]W.T. Winberry Jr., R. Riggin, R.G. Lewis, Compendium Method TO-4A: Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD), U.S. Environmental Protection Agency, Cincinnati, OH, 1999.

[2]T. Colborn, F.S. vom Saal, A.M. Soto, Environ. Health Persp. 101 (1993) 378.

[3]D. MacKay, A. Fraser, Environ. Pollut. 110 (2000) 375.

Appendix A
Standard Operating Procedure: XAD-2 Cleaning Procedure Using the Dionex Accelerated Solvent Extractor 300

1 Method Summary

This method describes the procedures used to clean Amberlite XAD-2 resin using five solvents sequentially in the Dionex Accelerated Solvent Extractor 300.

2 Scope and Application

This SOP is part of an effort to update the TO-4A method, "Determination of pesticides and PCBs in ambient air using high volume PUF sampling followed by gas chromatographic/multi-detector detection," to utilize improved instrumentation. This method details the cleaning procedure for XAD-2 resin (Supelco/Aldrich Cat. no. 10357 or similar) to be used for sampling semivolatile organic compounds from environmental matrices, such as air and water. This SOP assumes that the ASE and peripheral devices are properly installed and functioning.

3 Personnel Qualifications

This SOP is written for users who have experience keeping a laboratory notebook and operating the Dionex 300. The operator should have a background in science with laboratory experience and must be trained by experienced personnel before undertaking these techniques. The operator must be able to understand the information in the operating manuals and the SOPs related to this procedure.

4 Health and Safety

Standard laboratory protective clothing is required at all times during chemical operations in accordance with a health and safety research protocol. Operations involving the handling of solvents should be performed under a fume hood. Use caution when removing ASE cells from the carousel after extraction, as they may be hot.

5 Definitions, Acronyms, and Abbreviations

ASE	accelerated solvent extractor
ECD	electron capture detector
GC	gas chromatograph
L	liter
l to r	left to right
min	minute
mL	milliliter
MS	mass spectrometry
PCB	polychlorinated biphenyl
PEEK	polyetheretherketone
psi	pounds per square inch
PUF	polyurethane foam
s	second
SOP	standard operating procedure

6 Equipment and Supplies

Filter insertion tool
Aluminum funnel
Scoopula
2 L Dionex solvent bottles
Sample logbook
Glass fiber filters (Part # 056781 or similar)
Large, flat-bottomed flask
Large beaker
Laboratory notebook
Chemical fume hood
Dionex instruction manual
Dionex 300 with solvent controller and peripheral devices
Personal computer with AutoASE software
100 mL ASE cells, end caps, and components (Part # 068101)
250 mL Dionex collection bottles with lids and septa
Blank matrix cleaning notebook
Pesticide grade solvents: acetone, hexane, methanol, and dichloromethane
Rotary or nitrogen evaporator
Clean amber jars with Teflon lined lids
Personal protective equipment (gloves, safety glasses or goggles, and lab coat)
XAD-2 resin 20-60 mesh, 1.02 g/mL density, 90 Å mean pore size, 300 m^2/g surface area (Supelco/Aldrich Cat. #10357 or similar)

7 Procedure

NOTE: It is important for all users to read the entire SOP before beginning any of the procedure and to ask questions if any of the instructions are unclear.

XAD-2 resin will be placed into clean 100 mL ASE cells and cleaned using the following the procedure.

7.1 Cell assembly

It is assumed that the end caps have already been assembled. For additional information on assembly and filling of Dionex 300 cells please refer to the instruction manual or an operation SOP for this instrument. This procedure should be performed while wearing nitrile gloves. Select the desired number of 100 mL ASE cells for filling with XAD-2.

1. Check the PEEK seals (orange rings inside endcap) and O-rings (small white at entrance/exit of end cap) for excessive wear and replace if necessary.
2. Screw bottom end cap in place to hand tight. (The bottom of the cell is the end without the Dionex symbol and cell ID number.)
3. Insert the glass fiber filter with the filter insertion tool.

7.2 Filling the cells with XAD-2

NOTE: No more than twelve cells can be loaded onto the instrument at one time.

1. Insert the aluminum funnel in the top of the cell.
2. Using a scoopula, add 2 to 3 scoopfuls of XAD to the cell. **NOTE**: Be very cautious during this step. If any XAD spills into the bottom endcap, it may prevent proper sealing and cause the cell to leak during extraction.
3. Tamp down the XAD in the cell by *gently* tapping the cell on a counter top.
4. Repeat steps 3 and 4 until the cell becomes half full.
5. Use the black filter insertion tool to tamp down the XAD. Continue to add XAD and tamp it down with the insertion tool until the level of XAD is approximately 1-2 in from the top of the cell.
6. Remove the aluminum funnel and insert a glass fiber filter on top of the XAD.
7. Screw the top endcap in place to hand tight. (The top of the cell is the end with the Dionex symbol and cell ID number.)
8. Check the endcaps and outside of the cell for extraneous XAD. If present, thoroughly remove it.
9. Repeat steps 1 through 9 until all cells are filled.

7.3 Preparing the instrument

1. Check air and nitrogen gas tank ON/OFF state and pressure. (Tanks should be on and pressure >200 psi.)
2. Check system pressure gauges (l to r).
   a. Solvent bottle 5-10 psi
   b. Air pressure 50 psi
   c. Oven compression 130 psi
5. Check solvent levels in all solvent bottles and fill if needed (see Figure E2. Column packing.
4. Empty waste bottle and dispose of waste in accordance with waste management procedures.
5. Empty collection rinse bottle and replace septa if necessary. The septa should be changed every two to three runs.
6. Check hydrocarbon sensor.
   a. On the front panel of the Dionex 300, proceed to the "Menu of Screens."
   b. Push 7 for the "Diagnostic menu."
   c. Push 4 for the "Hydrocarbon calibration."
   d. Reading should be between 1000 and 4000. If not, refer to the Dionex 300 manual for adjustment.
   e. When finished, push the menu button to exit. *Do not push "Enter" to calibrate.*
7. Perform rinse to check solvent flow. Carefully listen to the pump to insure it is operating correctly. If the pump sounds abnormal, try performing additional rinses until the solvent lines have filled and the pump sounds normal. If the sound does not return to normal, do not use the instrument until it has been checked by a Dionex Service Representative and is fixed.

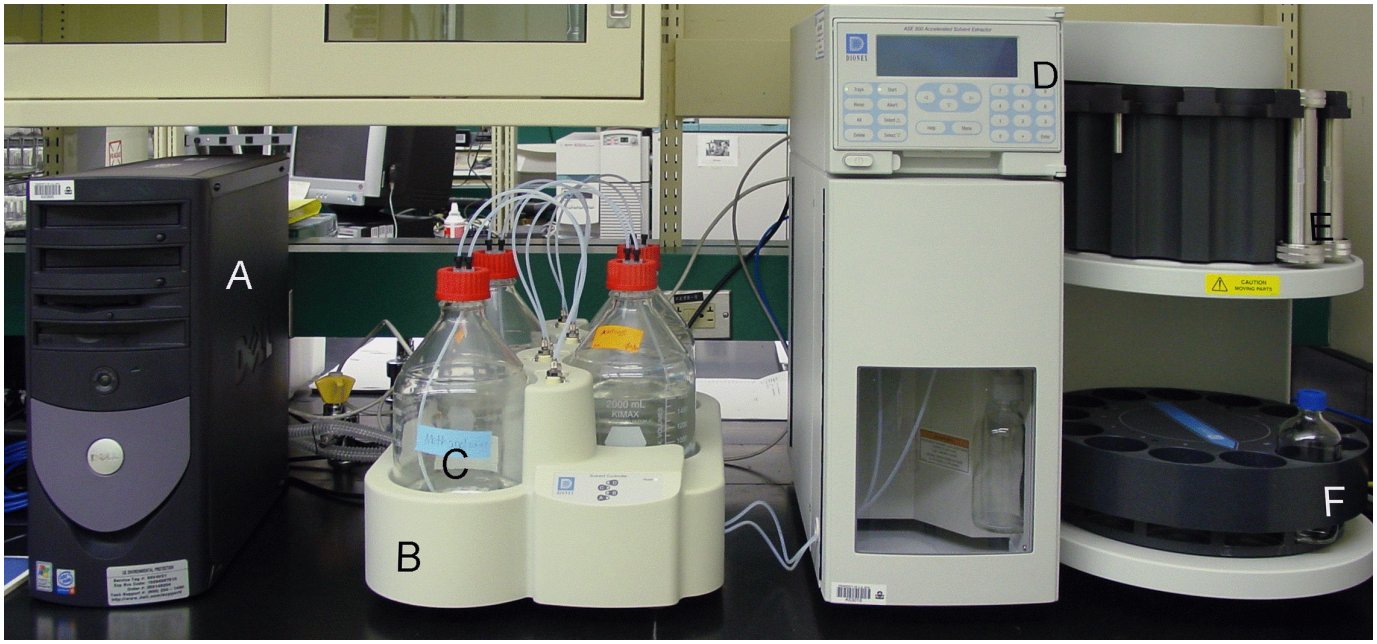

Figure A1. Dionex 300 system: (A) PC with AutoASE software, (B) solvent controller, (C) solvent reservoir, (D) keypad and display, (E) 100 mL cells, and (F) collection bottle.

8. Check the cells and cell caps for gouges, worn seals, and XAD particles.
9. Place the ASE cells into the top carousel. Use caution when rotating the tray. Make sure it is unlocked and moves freely.
10. Place the same number of clean bottles as cells into the bottom carousel.
11. Record the cell numbers, contents, method name, date, etc., in the sample logbook.
12. Record the activities in the Blank Matrix Cleaning notebook.

7.4 Preparing the method

Using the instructions in the Dionex 300 manual or an ASE operation SOP, enter the following method parameters in the AutoASE software.

Pressure: 1500 psi (preset at 1500 psi)
Temperature: 75 °C
Preheat time: 0 min
Purge during preheat: Off
Heat time: 5 min
Static time: 5 min
Flush volume: 50% (percent of total cell volume)
Purge time: 90 s
Static cycles: 1
Solvent composition: varies (see below)

One method needs to be prepared and saved with a unique name for each solvent/mixture listed below.

Solvents:

Method 1 - 100% Methanol

Method 2 - 100% Acetone

Method 3 - 100% Dichloromethane

Method 4 - 100% Hexane

Method 5 - 20% Acetone, 80% Hexane

7.5 Preparing the schedule

Using the instructions in the Dionex 300 manual or an ASE operation SOP, enter the schedule conditions in the AutoASE software.

1. Go to "EDIT" on the menu bar, then open "Schedule File." At this point, an existing schedule may be edited or a new schedule created. Set the parameters for the schedule as follows.
   a. BOTTLE: The order is preset from 1 to 12.
   b. CELL: The cell positions are labeled from 1 to 12. Up to 12 cells filled with XAD may be cleaned with each solvent. If the flush volume is changed to >50%, it is recommended that a maximum of 10 cells be used.
   c. METHOD FILE: In this box, place the name of the method to be used to extract the corresponding cell (e.g., Method 1, Method 2, etc.). Double-clicking on the box will reveal the method files. Double-click on the method to be used and it will be placed in the schedule box.
   d. RINSE: Off. The system is not rinsed after each cell is extracted.
   e. VOLUME: 0. The system is not rinsed after each cell is extracted.
   f. SAMPLE ID: In this space, include the sample name or code number.
2. Once the schedule has been completed, click "SAVE AS" and give the schedule a name. After the schedule has been named, click "EXIT".
3. Go to "FILE" on the menu bar, then to "Load Schedule."
4. Select the schedule just created from the list and either double-click on the name or click "OK". The schedule is now loaded.
5. Go to "RUN" on the menu bar and select "START". The Dionex 300 will automatically run the schedule after a preprogrammed rinse. Nine (9) mL of solvent will be used to rinse the system prior to the first cell being extracted.

7.6 After a schedule is complete

1. Check solvent levels in all solvent bottles and fill if needed.
2. After each extraction cycle, hand tighten the endcaps on each cell. Use caution when handling cells, as they will be hot from the oven. Allow 10-15 min for the cells to cool.
3. Check the cells and cell caps for XAD particles and remove them if present.
4. Replace the cells into the same location on the top carousel.
5. Empty the solvent collection and rinse bottles into an appropriate waste container.
6. Check the septa on the collection bottles and replace them every two extractions/schedules. Check the septa on the rinse bottle and replace it every five to six extractions/schedules.
7. Replace the solvent collection bottles in the bottom carousel.
8. Using AutoASE, load the schedule for the next method.
9. Repeat steps 1 through 8 until all five methods are complete.

7.7 After all schedules are complete

1. The Method 5 extracts should be reduced in volume by rotary and/or nitrogen ev aporation.

2. The resulting extracts should be treated as samples and analyzed by GC/ECD (or GC/MS) using the same method by which samples are analyzed.
3. Non-quantifiable levels of the analytes of interest are required. The exact concentration of non-quantifiable levels will vary depending on the methods and instrumentation used for analysis. Record this analysis in the appropriate laboratory notebook and the Blank Matrix Cleaning notebook.
4. The XAD just cleaned must be dried before storage by one of the methods below. Dry XAD will be free flowing and no longer smell of solvents.
    a. Pour clean XAD into a large beaker, label the beaker, and place it in a fume hood overnight.
    b. Pour clean XAD into a large flat-bottom flask and proceed with roto-vapping until no more solvent is being removed (watch for drips into the collection vessel under the condenser).
5. Once dried, the XAD should be placed in amber jars, capped, labeled, and stored at room temperature until used.

8 Data and Records Management

Data and records management issues are discussed throughout the procedure. Data will be recorded promptly, legibly, and in permanent ink in the logbook and in laboratory notebooks designated for each instrument and project. Electronic data files related to the project should be noted in the laboratory notebook. A logbook containing pertinent information is kept to record samples extracted on the Dionex 300. A separate notebook is used to record the activities pertaining to the cleaning of matrices that are to be used as matrix blanks.

9 Quality Control and Quality Assurance

Quality assurance and control issues are discussed throughout the procedure. Following XAD cleaning procedure, the last extracts will be analyzed as samples. Non-quantifiable levels of the compounds of interest are required for the batch's acceptance as clean XAD.

10 Waste Management

Solid, liquid, and glass waste are disposed of in separate containers. Solvents and samples used in this procedure should be disposed according to health and safety regulations and with appropriate labeling and recordkeeping.

11 References

Dionex 300 Accelerated Solvent Extractor Operator's Manual. Dionex Corporation, 2000. Revision 01.

Appendix B
Standard Operating Procedure: Preparation and Packing of ASE Cells for Air Sampling with XAD-2

1 Method Summary

This method describes the procedures needed for preparing stainless steel accelerated solvent extraction (ASE) cells for air sampling. This includes instructions for inserting the snap rings, retaining screens, and XAD-2 resin.

2 Scope and Application

This SOP is part of an effort to update the TO-4A method, "Determination of pesticides and PCBs in ambient air using high volume PUF sampling followed by gas chromatographic/multi-detector detection." Updates include stainless steel sampling cartridges that can be extracted by an automated ASE, XAD-2 resin sorption bed, and mass spectrometry. This document describes how to prepare modified 100 mL cells for air sampling based on the TO-4A method. The cells must have been modified previously with four grooves to retain 4 in of XAD-2 resin with screens and snap rings. XAD-2 resin must be cleaned prior to cell assembly. After assembly, the cells will be ready for air sampling.

3 Personnel Qualifications

This SOP is written for users who have experience keeping a laboratory notebook and operating the Dionex 300 and sampling apparatus. The operator should have a background in science with laboratory experience and must be trained by experienced personnel before undertaking these techniques. The operator must be able to understand the information in operating manuals and the SOPs related to this procedure. It is important for all users to read the entire SOP before beginning any of the procedure and to ask questions if any of the instructions are unclear.

4 Health and Safety

Standard laboratory protective clothing is required at all times during chemical operations in accordance with a health and safety research protocol. Use caution when manipulating the snap rings, as they may suddenly release a large amount of tension and cause injury. Safety glasses are essential during this procedure. Secure loose personal items (especially long hair) and clothing when working around the vacuum pumps to prevent injury. If present, remove the Teledyne Hastings flow controller from the sampling train during this operation to ensure that XAD resin does not enter and damage the equipment.

5 Definitions, Acronyms, and Abbreviations

ASE	accelerated solvent extraction
mL	milliliter
g	gram
PCB	polychlorinated biphenyl
PUF	polyurethane foam

6 Equipment and Supplies

- 100 mL ASE cells with two sets of grooves machined 4 in apart
- Two ASE cell endcaps per cell
- Two retaining screens per cell
- Four snap rings per cell
- Adjustable spanner wrenches
- Dionex 300 with solvent controller and peripherals
- Dionex 300 cell funnel or equivalent
- Dionex 300 insertion tool or equivalent plunger
- Flat-bladed screw driver
- Gast vacuum pump Model 0523-101Q-SG588DX or equivalent
- High-purity acetone
- Modified sampling mount (University of Georgia Machine Shop, see Figure B4)
- Personal protective equipment (gloves, safety glasses or goggles, and lab coat)
- Precleaned XAD-2 resin (~25 g per cell)
- SOP "XAD-2 cleaning procedure utilizing the Dionex Accelerated Solvent Extractor 300"

7 Procedure

7.1 Assembling snap rings #1, #2, and #3

Collect all necessary equipment for cell assembly. Figure B1 shows the components of the ASE cell for reference. Figure B2 shows the inside of a cell with one set of grooves for the snap rings.

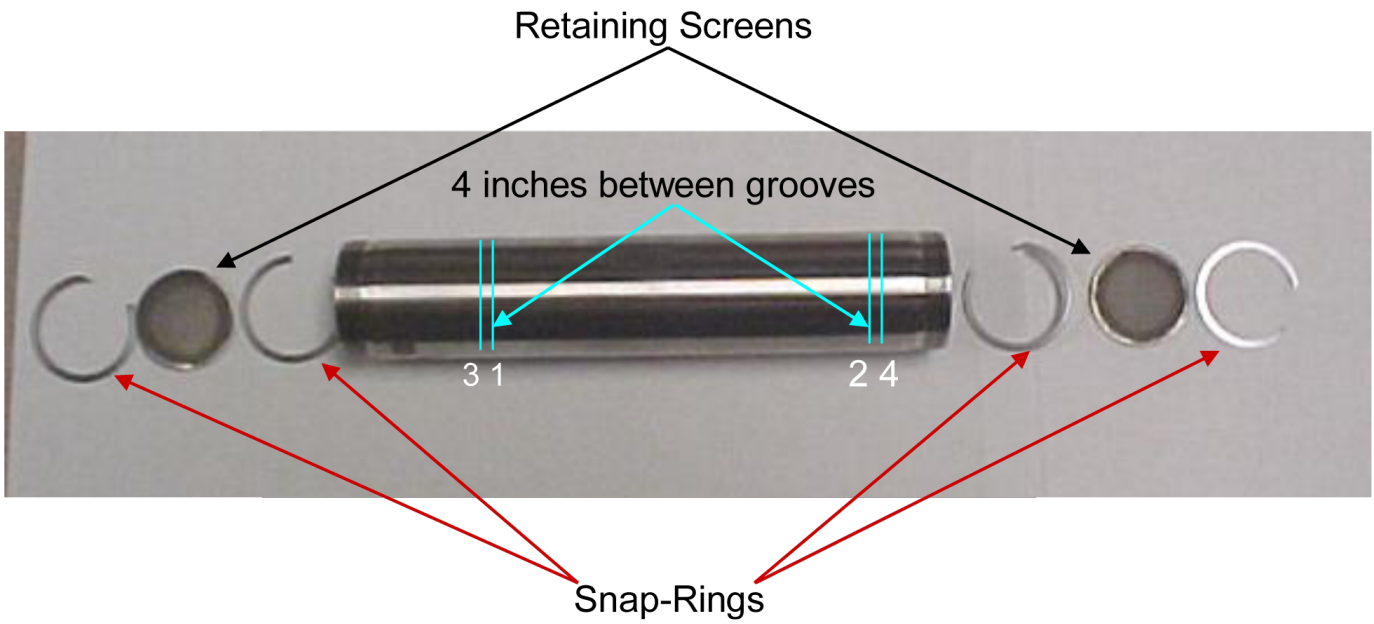

Figure B-1. Linear view of modified ASE cell, snap rings, and retaining screens. Blue grooves are numbered based on the recommended snap-ring-insertion order.

Figure B-2. End view of modified ASE cell showing location of grooves #2 and #4.

Following the diagram in Figure B3, place the filter insertion tool in the cell just below groove #1.

6. Turn snap ring #1 perpendicular to the grooves, and insert it into the cell. Lower the snap ring past groove #1.
7. Using your fingers, a flat-bladed screwdriver, and/or the insertion tool, slowly turn the snap ring so it fits into groove #1.
8. Remove the filter insertion tool from the cell.
9. Place snap ring #2 into the cell perpendicular to the grooves.
10. Lower it past groove #2 in the perpendicular orientation and then slowly pull it back towards the groove. The snap ring should turn and slide into the groove.
11. Place a screen flat on top of snap ring #1, noting the orientation of the open section of the snap ring. The filter insertion tool may need to be used to make sure the screen is flat on top of the snap ring.
12. Once the screen is in place, insert snap ring #3 perpendicularly into the cell and turn the open section opposite the open section of snap ring #1. The idea is to make sure that the two open portions DO NOT align.
13. Using your fingers or the filter insertion tool, push the snap ring into groove #3. Use the flat-bladed screwdriver to change the orientation of the open portion of the snap ring if necessary.

7.2 Packing the XAD resin

1. Orient the cell so that the screen between grooves #1 and #3 is on the bottom, and screw the cell onto the modified sampling mount.
2. If necessary, remove the flow controller from the sampling train using adjustable wrenches.
3. Attach the modified sampling mount and cell onto the sampler and tighten the associated fittings. See Figure B4 for proper setup.
4. Plug in the Gast vacuum pump, which will turn on immediately.
5. Place the cell funnel into the open end of the ASE cell.

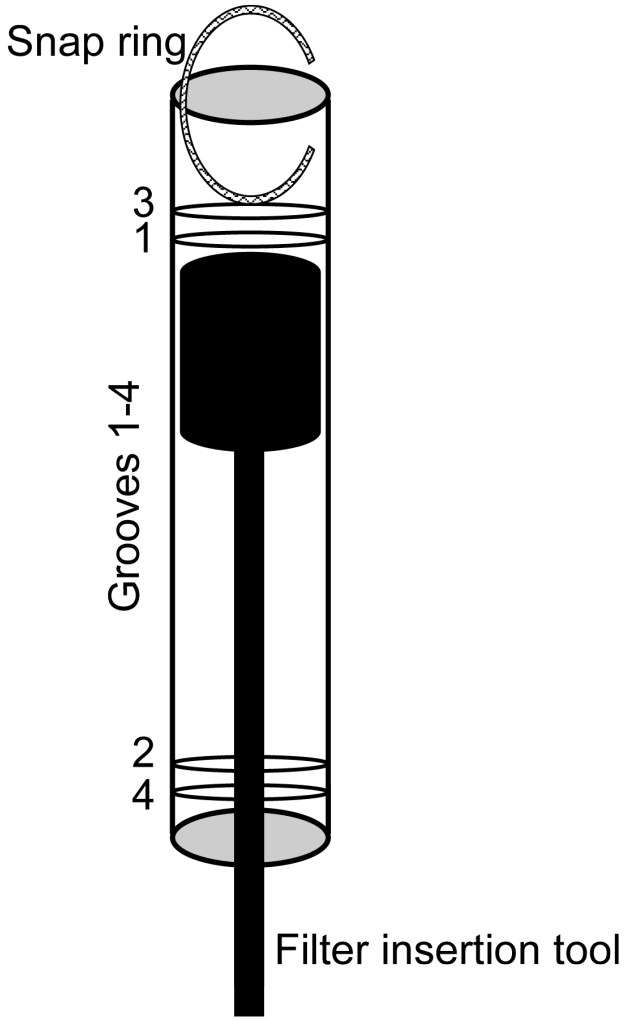

Figure B-3. Schematic for insertion of snap ring 1. Ring should be oriented vertically with the axis of the cell.

6. Slowly pour the pre-cleaned XAD-2 resin into the funnel. This operation should be done near an open fume hood, as the XAD will likely give off acetone fumes. Continue to fill the cell until the level of XAD is just below snap ring #2. Gentle tapping may be required to level the XAD.
7. Pack the cell as close to the ring as possible. Ensure that the snap ring is free of XAD particles, as this will provide a poor seal with the screen and may cause leaking of XAD. Fingers, a brush, or laboratory wipe can be used to clean the snap ring.
8. Unplug the vacuum pump to turn it off.
9. After the last cell is filled, replace the flow controller in the sampling train using adjustable wrenches.

7.3 Inserting snap ring #4

1. Place a screen flat on top of snap ring #2, noting the orientation of the open section of the snap ring. The filter insertion tool may be needed to make sure the screen is flat on top of the snap ring.

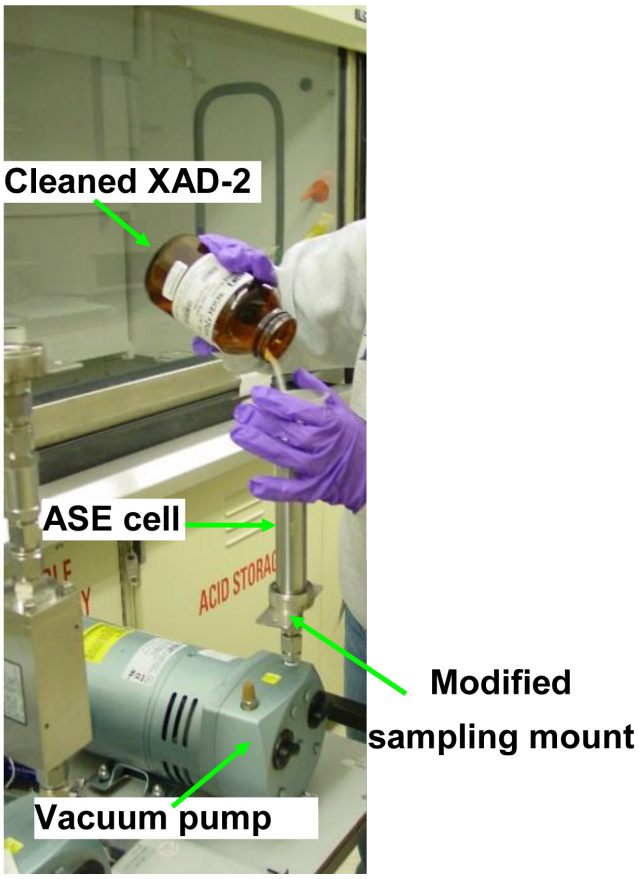

Figure B-4. Filling the ASE cell using the modified sampling mount, vacuum pump, and cleaned XAD-2 resin.

2. Once the screen is in place, insert snap ring #4 perpendicularly into the cell and turn the open section opposite the open section of snap ring #2. The idea is to make sure that the two open portions do NOT line up.
3. Using your fingers or the filter insertion tool, push the snap ring into groove #4. Use the flat-bladed screwdriver to change the orientation of the open portion of the snap ring if necessary.
4. Screw endcaps onto both ends of the ASE cell for storage.
5. Record these actions in a laboratory or project notebook. Repeat the entire procedure for each cell to be packed.

7.4 Reusing cells

1. Once the cells have been packed with XAD-2 resin, it is generally not necessary to replace the XAD between samples if proper extraction and cleanup steps are followed.
2. After extraction of the cartridges and just prior to the next sampling event, each cell must be extracted by the Dionex 300 with 100% acetone. This step is detailed in the SOP "XAD-2 Cleaning Procedure Utilizing the Dionex Accelerated Solvent Extractor 300."

3. The extract from this 100% acetone extraction must be analyzed prior to the next sampling event. If detectable concentrations of analytes are found, it may be time to pack the cell with new XAD-2 resin.

8 Data and Records Management

Data and records management issues are discussed throughout the procedure. Data will be recorded promptly, legibly, and in permanent ink in the logbook and in laboratory notebooks designated for each instrument and project. Record the cell number and packing date in a laboratory notebook. A logbook containing pertinent information is kept to record samples extracted on the Dionex 300. A separate notebook is used to record the activities pertaining to the cleaning of matrices that are to be used as matrix blanks.

9 Quality Control and Quality Assurance

QA/QC is discussed throughout this document, but additional parameters are listed below. At a minimum, one sampling blank (with air, no spiking solutions), one sample duplicate (with air, no spiking solutions), and one QA spike (no air, GC and LC spiking solutions added) are included for each sampling event and should be analyzed together. The procedures in this SOP are in preparation for a sampling event, so enough cells must be packed to accommodate required QC samples.

10 Waste Management

Generally, waste is not generated by this procedure. Solid, liquid, and glass waste are disposed of in separate containers. Solvents and samples used in this procedure should be disposed according to health and safety regulations, and with appropriate labeling and record keeping.

11 References

SOP “XAD-2 Cleaning Procedure Utilizing the Dionex Accelerated Solvent Extractor 300.”

Appendix C
Standard Operating Procedure: Air Sampling with ASE Cells

1 Method Summary

This method describes the procedures needed for collecting air samples using stainless steel accelerated solvent extraction (ASE) cells packed with XAD-2 resin. It includes instructions on the last cleanup step for the XAD, sampler setup, and the use of flow controllers during the sampling period.

2 Scope and Application

This SOP is part of an effort to update the TO-4A method, "Determination of pesticides and PCBs in ambient air using high volume PUF sampling followed by gas chromatographic/multi-detector detection." Updates include stainless steel sampling cartridges that can be extracted by an automated ASE, XAD-2 resin sorption bed, and mass spectrometry. This SOP is followed when collecting air samples using modified ASE cells with XAD-2 resin packing material. It is assumed that the cells have already been assembled and packed with XAD-2 resin and that the ASE and peripheral devices are properly installed and functioning. The compounds listed in Table C1. GC and LC target analytes are the target analytes for this method.

3 Personnel Qualifications

This SOP is written for users who have experience keeping a laboratory notebook and operating the Dionex 300 and sampling apparatus. The operator should have a background in science with laboratory experience and must be trained by experienced personnel before undertaking these techniques. The operator must be able to understand the information in operating manuals and the SOPs related to this procedure. It is important for all users to read the entire SOP before beginning any of the procedure and to ask questions if any of the instructions are unclear.

4 Health and Safety

Standard laboratory protective clothing is required at all times during chemical operations in accordance with a health and safety research protocol. Use caution when manipulating the snap rings, as they may suddenly release a large amount of tension and cause injury. Safety glasses are essential during this procedure. Secure loose personal items (especially long hair) and clothing when working around the vacuum pumps to prevent injury. The toxicity or carcinogencity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard, as most are pesticides. The following compounds are on the "P" list and should be handled only in a fume hood with proper personal protective equipment: aldrin, dieldrin, heptachlor, and methyl parathion. "P" coded compounds (acutely toxic) must also be disposed of separately. Please check with laboratory or safety personnel on proper disposal of these compounds.

Table C1. GC and LC target analytes

GC target analytes			
Alachlor	Aldrin	Atrazine	Captan
cis-Chlordane	*trans*-Chlordane	Chlorothalonil	Chlorpyrifos
2,4-D ethyl ester	2,4-D methyl ester	Dacthol	*p,p'*-DDE
o,p'-DDT	*p,p'*-DDT	Diazinon	Dicloran (Botran)
Dieldrin	Ethyl parathion	Fenchlorphos (Ronnel)	Folpet
a-HCH	b-HCH	Heptachlor	Heptachlor epoxide B
Hexachlorobenzene	Lindane (g-HCH)	Malathion	Methyl parathion
Methoxychlor	Metolachlor	Mirex	*trans*-Nonachlor
Oxychlordane	Propazine	Simazine	Trifluralin
LC target analytes			
Allethrin	Atrazine	Bendiocarb	Carbaryl
Carbofuran	Chlortoluron	Cinerin I & II	Diazinon
Diuron	Dicrotophos	Fenvalerate	Fluometuron
Jasmolin I & II	Linuron	Monuron	*o*-Phenylphenol
cis-Permethrin	*trans*-Permethrin	Propazine	Propoxur (Baygon)
Pyrethrin I &II	Resmethrin	Simazine	Tebuthiuron

5 Definitions, Acronyms, and Abbreviations

ng	nanogram
mL	milliliter
min	minute
h	hour
m^3	cubic meter
µL	microliter
s	second
µg	microgram
PUF	polyurethane foam
L	liter
LC	liquid chromatography
GC	gas chromatography
ASE	accelerated solvent extraction
SOP	standard operating procedure
QA/QC	quality assurance/quality control
psi	pounds per square inch
PCB	polychlorinated biphenyl
HCH	hexachlorocyclohexane
DDT	dichlorodiphenyltrichloroethane
DDE	dichlorodiphenyldichloroethylene

6 Equipment and Supplies

- 100 µg/mL stock solutions of target analytes (see Table C1. GC and LC target analytes for analyte list)
- 100 mL modified ASE cells packed with cleaned XAD-2 resin
- Two ASE cell endcaps per cell
- 25 mL volumetric flask and stopper
- Dionex 300 with solvent controller and peripherals
- Clock
- Eppendorf pipet 100-1000 mL with tips
- Gast vacuum pump Model 0523-101Q-SG588DX or equivalent
- High-purity (pesticide grade or better) ethyl acetate and acetone
- Laboratory notebook
- Mass flow controller
- Modified sampling mount
- Personal computer with AutoASE software
- Personal protective equipment (gloves, safety glasses or goggles, and lab coat)
- SOP "XAD-2 cleaning procedure utilizing the Dionex Accelerated Solvent Extractor 300"
- THPS-100 Power supply and readout

7 Procedure

7.1 Preparation of the sampling cells

Use SOP "XAD-2 cleaning procedure utilizing the Dionex Accelerated Solvent Extractor 300" as reference materials for the following procedure.

1. Load/create method in the AutoASE software with the following parameters.

Pressure: 1500 psi (preset at 1500 psi)
Temperature: 75 °C
Preheat time: 0 min
Purge during preheat: Off
Heat time: 5 min
Static time: 5 min
Flush volume: 50%
Purge time: 180 s
Static cycles: 1
Solvent composition: 100% acetone

2. Using a sequence, run this cleaning method for each cell that will be used during the sampling event. Be sure to include enough cells for QA/QC samples. The minimum requirement per sampling event is one blank, one duplicate, and one spike.
3. Dispose of the acetone waste in an appropriately labeled container and record the addition on the waste log sheet.

7.2 Preparation of the spiking solutions

1. It is not necessary to make new spiking solutions for each sampling event. If the spiking solutions are already prepared, remove them from freezer storage and allow them to reach room temperature.
2. If new spiking solutions need to be made, prepare one spiking solution for all GC target analytes in ethyl acetate (400 ng/mL). This can be accomplished for a variety of final volumes, but the suggested method follows.
    - Prepare a solution of all GC target analytes by diluting 100 mL of each 100 µg/mL stock standard to 25 mL with ethyl acetate.
3. Prepare one spiking solution for all LC target analytes in ethyl acetate (400 ng/mL). This can be accomplished for a variety of final volumes, but the suggested method follows.
    - Prepare a solution of all LC target analytes by diluting 100 mL of each 100 µg/mL stock standard to 25 mL with ethyl acetate.
4. Label spiking solutions with the solution name, concentration, solvent, date made, expiration date (1 year from date made), and preparers initials.

7.3 Preparation of sampler

1. The sampler (vacuum pump, flow controller, controller power supply, and modified sampler mount) should be assembled as displayed in Figure E2. Column packing..

2. Screw the XAD-2 packed cell onto the modified sampling mount with the screen closest to the cell threads pointing up and the Dionex symbol and cell number at the bottom.
3. For each sampler unit, plug in the controller power supply and allow it to warm up for at least 30 min.
4. Label each sampling cell with the date, analyst's initials, and sample identification.
5. After the waiting period, check the display on the controller power supply (see Figure C2. Front panel of controller power supply.). The display should read zero. If it does not read zero, press and hold the "zero" button until it resets (~5 s).

7.4 Air sampling

This procedure has been used only in a laboratory setting during method development activities. Adjustments will be required if this method and procedure are used in a field setting. Specifically, the sampling time and volume of air must be considered. The TO-4A method calls for a 24-h sample of 300 m^3 of air. This sampling apparatus will sample 40-60 m^3 of air per day, so one must decide to match the time (24 h) or the volume of air sampled (~6 days).

1. Be sure to include QA/QC samples, such as blanks, duplicates, and spikes. At a minimum, one sampling blank (with air, no spiking solutions), one sample duplicate (with air, no spiking solutions), and one QA spike (no air, GC and LC spiking solutions added) are included for each sampling event.
2. Plug in the vacuum pumps. They should start immediately.

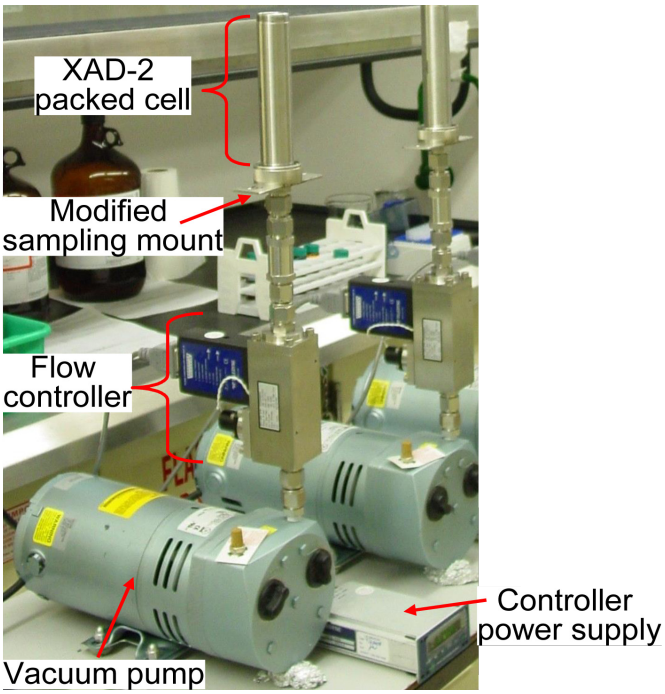

Figure C1. Air sampling unit assembly.

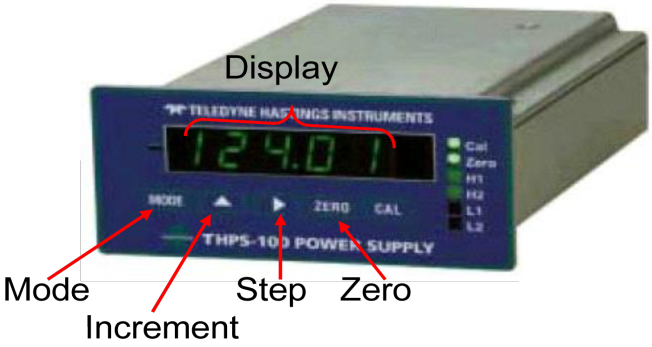

Figure C2. Front panel of controller power supply.

3. Using the buttons on the controller power supply (see Figure C2. Front panel of controller power supply.), set the flow to 100 L/min. Push the "MODE" button, then the 5 "increment" button, and then the4 "step" button (until the first digit is 1). Push the "ZERO" button to exit.
4. The display and flow will begin to increase slowly, reaching a maximum in <1 min. The flow will be approximately 30 L/min with the XAD cartridge attached. Record the sampler start time in the laboratory notebook from a laboratory or personal clock.
5. Record the beginning flow rate in the laboratory notebook for each sampler.
6. Prepare the QA spike sample by removing the top endcap (near Dionex symbol and cell number) from a XAD cartridge and add 0.5 mL each of the 400 ng/mL GC and LC spiking solutions with an Eppendorf pipet onto the XAD through the stainless steel screen to produce a 200 ng/sample concentration. Replace the endcap and store this sample near the vacuum pumps. Record these actions in the laboratory notebook.
7. Additional measurements of the flow rate can be recorded in the laboratory notebook if desired.
8. Allow the sampler to run for 24 h. Approximately 40-60 m^3 will be collected. Longer time periods may be required for different experimental goals.
9. After the sample has been collected, record the ending flow rate and sampler stop time in the laboratory notebook using the same laboratory or personal clock as in step 4.
10. Unplug the samplers, followed by the controller power supplies.
11. Remove the modified ASE cartridges and screw endcaps on to both ends.
12. Calculate the total volume of air sampled using the equation below and record the results in the laboratory notebook.

$$Volume(m^3) = \frac{Flow_{Avg}(L)}{(\min)} \times \frac{60(\min)}{1(h)} \times \frac{Samplingtime(h)}{} \times \frac{1(m^3)}{1000(L)}$$

8 Data and Records Management

Data and records management issues are discussed throughout the procedure. Data will be recorded promptly, legibly, and in permanent ink in the logbook and in laboratory notebooks designated for each instrument and project. For each sampler, the start and stop times must be recorded in a laboratory notebook. Corresponding flow controller readings should be taken at the beginning and end of the sampling period and recorded along with the ASE cell number. Descriptive information of the sample should also be included (spike, duplicate, date, location, etc.). Electronic data files related to the project should be specified in the laboratory notebook. A logbook containing identifying information (sample name, date, cell number, analyst initials, method, and sequence names) is kept to record samples extracted on the Dionex 300. A separate notebook is used to record the activities pertaining to the cleaning of matrices that are to be used as matrix blanks.

9 Quality Control and Quality Assurance

Quality assurance and control issues are discussed throughout the procedure. At a minimum, one sampling blank (with air, no spiking solutions), one sample duplicate (with air, no spiking solutions), and one QA spike (no air, GC and LC spiking solutions added) are included for each sampling event.

10 Waste Management

Solid, liquid, and glass waste are disposed of in separate containers. Solvents and solids used in this procedure should be disposed according to health and safety regulations and recorded on waste logsheets. Several compounds used in this method (aldrin, dieldrin, heptachlor, and methyl parathion) are to be disposed of separately with “P” coded waste.

11 References

Teledyne Hastings Instruments instruction manual Mass flowmeter, controller readout THPS-100, Document Number 161-112005, Revision 05, November 2005.

Instruction manual for THPS-100 Power supply and readout, Revision 05, November 2005.

SOP “XAD-2 cleaning procedure utilizing the Dionex

Accelerated Solvent Extractor 300.”

Appendix D
Standard Operating Procedure: Extracting TO-4A Air Samples with the Dionex ASE 300

1 Method Summary

This method describes the procedure for extracting selected TO-4A pesticides from air samples collected in stainless steel accelerated solvent extraction (ASE) cells containing XAD-2 resin, including instructions for the adding surrogate standards, ASE extraction, and rotary evaporation.

2 Scope and Application

This SOP is part of an effort to update the TO-4A method, "Determination of pesticides and PCBs in ambient air using high volume PUF sampling followed by gas chromatographic/multi-detector detection." Updates include stainless steel sampling cartridges that can be extracted by an automated ASE, XAD-2 resin sorption bed, and mass spectrometry. This SOP is used to extract and reduce air samples after collection using modified ASE cells with XAD-2 resin packing material. It is assumed that the ASE and peripheral devices are properly installed and functioning. The compounds listed in Table D1. GC and LC target analytes and GC surrogates are the target analytes and surrogate standards for this method.

3 Personnel Qualifications

This standard operating procedure is written for users who have experience keeping a laboratory notebook and operating the Dionex 300 and rotary evaporator. The operator should have a background in science with laboratory experience and must be trained by experienced personnel before undertaking these techniques. The operator must be able to understand the information in operating manuals and the SOPs related to this procedure.

4 Health and Safety

Standard laboratory protective clothing is required at all times during chemical operations in accordance with a health and safety research protocol. Operations involving the handling of solvents should be performed under a fume hood. The toxicity or carcinogencity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard, as most are pesticides. The following compounds are on the "P" list and should be handled only in a fume hood with proper personal protective equipment (PPE): aldrin, dieldrin, heptachlor, and methyl parathion. "P" coded (acutely toxic) compounds also must be disposed of separately. Please check with laboratory or safety personnel on proper disposal of these compounds. Use caution when removing ASE cells from the carousel after extraction, as they may be hot.

Table D1. GC and LC target analytes and GC surrogates

GC target analytes			
Alachlor	Aldrin	Atrazine	Captan
cis-Chlordane	*trans*-Chlordane	Chlorothalonil	Chlorpyrifos
2,4-D ethyl ester	2,4-D methyl ester	Dacthol	*p,p'*-DDE
o,p'-DDT	*p,p'*-DDT	Diazinon	Dicloran (Botran)
Dieldrin	Ethyl parathion	Fenchlorphos (Ronnel)	Folpet
a-HCH	b-HCH	Heptachlor	Heptachlor epoxide B
Hexachlorobenzene	Lindane (g-HCH)	Malathion	Methyl parathion
Methoxychlor	Metolachlor	Mirex	*trans*-Nonachlor
Oxychlordane	Propazine	Simazine	Trifluralin
GC Surrogate standard compounds			
^{13}C Atrazine	D_{10} Chlorpyrifos	D_{10} Diazinon	Heptachlor epoxide A
LC target analytes			
Allethrin	Atrazine	Bendiocarb	Carbaryl
Carbofuran	Chlortoluron	Cinerin I & II	Diazinon
Diuron	Dicrotophos	Fenvalerate	Fluometuron
Jasmolin I & II	Linuron	Monuron	*o*-Phenylphenol
cis-Permethrin	*trans*-Permethrin	Propazine	Propoxur (Baygon)
Pyrethrin I &II	Resmethrin	Simazine	Tebuthiuron

5 Definitions, Acronyms, and Abbreviations

µg	microgram
µL	microliter
ASE	accelerated solvent extraction
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
GC	gas chromatography
HCH	hexachlorocyclohexane
LC	liquid chromatography
min	minute
mL	milliliter
ng	nanogram
PCB	polychlorinated biphenyl
PPE	personal protective equipment
psi	pounds per square inch
PUF	polyurethane foam
QA/QC	quality assurance/quality control
s	second
SOP	standard operating procedure

6 Equipment and Supplies

- 100 µg/mL stock solutions of surrogate standard compounds (see Table D1. GC and LC target analytes and GC surrogates)
- 100 mL ASE cells used for air sampling through XAD-2 resin
- Two ASE cell endcaps per cell
- 25 mL volumetric flask and stopper
- 250 mL ASE collection bottles with lids and septa
- 250 mL flat-bottom flasks with stoppers
- Dionex 300 with solvent controller
- Sample logbook
- Eppendorf pipet 100-1000 mL with tips
- Heidolph rotary evaporator and associated equipment (or similar)
- High-purity (e.g., pesticide grade) ethyl acetate, acetone, and hexane
- Laboratory notebook
- Personal computer with AutoASE software
- Personal protective equipment (gloves, safety glasses or goggles, and lab coat)
- SOP "Air sampling with ASE cells"

7 Procedure

NOTE: It is important for all users to read the entire SOP before beginning any of the procedure and to ask questions if any of the instructions are unclear.

7.1 Preparation of the surrogate spiking solution

NOTE: Prior to sample analysis for both GC and LC compounds on the same extracts, a decision must be made regarding two standards added to the samples. $^{13}C_3$ Atrazine and D_{10} Diazinon *cannot* be used simultaneously as a surrogate for GC compounds and as an internal standard for LC compounds. The addition of these compounds prior to extraction will impact the internal standard quantitation by LC. A suggested compromise is to select one of these compounds as a GC surrogate and the other as an LC internal standard.

1. It is not necessary to make new surrogate spiking solution for each extraction event. If the surrogate spiking solution is already prepared, remove it from freezer storage and allow it to reach room temperature.
2. If a new spiking solution needs to be made, prepare one spiking solution for all GC surrogate standards in ethyl acetate (400 ng/mL). This can be accomplished for a variety of final volumes, but the suggested method follows.
   - Prepare a solution of all GC surrogate standards by diluting 100 mL of each 100-µg/mL stock standard to 25 mL with ethyl acetate.
3. Label spiking solutions with the solution name, concentration, solvent, date made, expiration date (1 year from date made), and preparer's initials.

7.2 Extraction of the sample cells

1. All samples, including QA/QC samples, are treated in the same way as environmental samples throughout this procedure. At a minimum, one sampling blank (with air, no spiking solutions), one sample duplicate (with air, no spiking solutions), and one QA spike (no air, GC and LC spiking solutions added) are included for each sampling event and should be extracted together. See SOP "Air sampling with ASE cells" for additional details.
2. Remove the top endcap from the ASE cell (near Dionex symbol and cell number).
3. Add 0.5 mL of the 400 ng/mL GC surrogate standards with an Eppendorf pipet onto the XAD through the stainless steel screen to produce a 200 ng/sample concentration.
4. Replace the endcap.
5. Repeat steps 2 through 4 for each ASE cell to be extracted.
6. Load the cells into the top carousel with the Dionex symbol at the top.
7. Label one 250 mL ASE collection bottle for each cell with the sampling date, analyst's initials, and sample identification information. Load these bottles into the bottom carousel.
8. Load/create method in the AutoASE software with the following parameters.

Pressure: 1500 psi (preset at 1500 psi)
Temperature: 75 °C
Preheat time: 0 min
Purge during Preheat: Off
Heat time: 5 min
Static time: 5 min
Flush volume: 100%
Purge time: 120 s
Static cycles: 1
Solvent composition: 20% acetone, 80% hexane

9. Prepare a sequence that will run this method for each sample, including QA/QC samples such as blanks, duplicates, and spikes. Save, load, and run the sequence.
10. Record these actions in both the laboratory notebook and the ASE sample logbook. Include sample identification, cell number, method and sequence name, date, and analyst.

7.3 Rotary evaporation

1. Label a 250 mL flat-bottom flask for each sample with the sampling date, analyst's initials, and sample identification information.
2. Remove the extract bottles from the lower ASE carousel.
3. Pour the extract from each sample into the corresponding flat-bottom flask.
4. Rinse the sample bottle three times with approximately 5 mL of hexane each time. Add the rinses to the sample's flat-bottom flask.
5. Using a rotary evaporator, evaporate the samples to dryness. Dryness is obtained when the condenser is no longer dripping solvent. **NOTE**: The rotary evaporator water bath temperature should not exceed 40 °C.
6. Stopper the sample and store at room temperature until Florisil cleanup. If the next procedure will not begin within 1 week, the stoppered sample flasks should be refrigerated.

8 Data and Records Management

Data and records management issues are discussed throughout the procedure. Data will be recorded promptly, legibly, and in permanent ink in the logbook and in laboratory notebooks designated for each instrument and project. Electronic data files related to the project must be specified in the laboratory notebook. A logbook containing identifying information (sample name, date, cell number, analyst initials, method, and sequence names) is kept to record samples extracted on the 300.

9 Quality Control and Quality Assurance

Quality assurance and control issues are discussed throughout the procedure. All samples, including QA/QC samples, are treated in the same way as environmental samples throughout this procedure. A solution containing four surrogate standards is added to each sample prior to extraction to quantify the recovery of compounds using this method.

10 Waste Management

Solid, liquid, and glass waste are disposed of in separate containers. Solvents and solids used in this procedure should be disposed according to health and safety regulations and recorded on waste logsheets. Several compounds used in this method (aldrin, dieldrin, heptachlor, and methyl parathion) are to be disposed of separately with "P" coded waste.

11 References

SOP "Air sampling with ASE cells."

Appendix E
Standard Operating Procedure: Florisil Column Cleanup for TO-4A Pesticides in Air Samples

1 Method Summary

This SOP describes the cleanup step needed for the analysis of selected TO-4A pesticides. A Florisil cleanup column is loaded with an air sample extract, and the target analytes are eluted with six solvents. Following sample elution, each fraction volume is measured and divided in half to accommodate GC and LC analysis. The samples are then evaporated to dryness prior to instrumental analysis.

2 Scope and Application

This SOP is part of an effort to update the TO-4A method, "Determination of pesticides and PCBs in ambient air using high volume PUF sampling followed by gas chromatographic/multi-detector detection." Updates include stainless steel sampling cartridges that can be extracted by an automated accelerated solvent extractor (ASE), XAD-2 resin sorption bed, and mass spectrometry. This SOP assumes that the samples have been reduced to dryness prior to this procedure, that the rotary evaporator is operational and ready for use, and that the samples will be split for both GC and LC analysis. This SOP is used to cleanup air extracts using Florisil and six solvent fractions. The samples are collected on Amberlite XAD-2 resin, although this cleanup procedure also may be appropriate for other matrices. All GC and LC target analytes and GC surrogates for this method are listed in Table E1. Target analytes and surrogate compounds analyzed by this method.

3 Personnel Qualifications

This SOP is written for users who have experience keeping a laboratory notebook and operating the rotary evaporator. The operator should have a background in science with laboratory experience and must be trained by experienced personnel before undertaking these techniques. The operator must be able to understand the information in operating manuals and the SOPs related to this procedure.

4 Health and Safety

Standard laboratory protective clothing is required at all times during chemical operations in accordance with a health and safety research protocol. Operations involving the handling of solvents should be performed under the fume hood. The toxicity or carcinogencity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard, as most are pesticides. The following compounds are on the "P" list and should be handled only in a fume hood with proper personal protective equipment: aldrin, dieldrin,

Table E1. Target analytes and surrogate compounds analyzed by this method

GC target analytes			
Alachlor	Aldrin	Atrazine	Captan
cis-Chlordane	*trans*-Chlordane	Chlorothalonil	Chlorpyrifos
2,4-D ethyl ester	2,4-D methyl ester	Dacthol	*p,p'*-DDE
o,p'-DDT	*p,p'*-DDT	Diazinon	Dicloran (Botran)
Dieldrin	Ethyl parathion	Fenchlorphos (Ronnel)	Folpet
a-HCH	b-HCH	Heptachlor	Heptachlor epoxide B
Hexachlorobenzene	Lindane (g-HCH)	Malathion	Methyl parathion
Methoxychlor	Metolachlor	Mirex	*trans*-Nonachlor
Oxychlordane	Propazine	Simazine	Trifluralin
GC surrogate standard compounds			
^{13}C Atrazine	D_{10} Chlorpyrifos	D_{10} Diazinon	Heptachlor epoxide A
LC target analytes			
Allethrin	Atrazine	Bendiocarb	Carbaryl
Carbofuran	Chlortoluron	Cinerin I & II	Diazinon
Diuron	Dicrotophos	Fenvalerate	Fluometuron
Jasmolin I & II	Linuron	Monuron	*o*-Phenylphenol
cis-Permethrin	*trans*-Permethrin	Propazine	Propoxur (Baygon)
Pyrethrin I &II	Resmethrin	Simazine	Tebuthiuron

heptachlor, and methyl parathion. "P" coded (acutely toxic) compounds must also be disposed of separately. Please check with laboratory or safety personnel on proper disposal of these compounds. The user may choose to wear a dust mask type respirator during the weighing and pouring of Florisil and sodium sulfate to decrease the amount of inhaled particles.

5 Definitions, Acronyms, and Abbreviations

ASE	accelerated solvent extraction
cm	centimeter
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
EtOAc	ethyl acetate
GC	gas chromatography
HCH	hexachlorocyclohexane
ID	inner diameter
LC	liquid chromatography
min	minute
mL	milliliter
mm	millimeter
Na_2SO_4	sodium sulfate
PCB	polychlorinated biphenyl
PUF	polyurethane foam
QA/QC	quality assurance/quality control
s	second
SOP	standard operating procedure

6 Equipment and Supplies

- 100 and 150 mL beakers
- 125 and 500 mL flat-bottom flasks and stoppers
- 250 mL glass reservoirs
- 5, 50, 100 and 250 mL graduated cylinders
- 6%, 15%, and 50% mixtures of EtOAc in hexane
- Acetone and hexane squirt bottles
- Aldrich Florisil reagent grade 60-100 mesh or equivalent, activated at 675 °C by the manufacturer
- Burdick & Jackson high purity solvents or equivalent: hexane, ethyl acetate, and acetone
- Dust gun or source of dry air
- Eppendorf pipet 100-1000 mL with tips
- GC target analyte spiking solution, 400 ng/mL in EtOAc (see SOP "Air sampling with ASE cells" for preparation instructions)
- Glass chromatography columns (45 mm × 1 mm ID) with Teflon stopcock and fitted with a glass frit
- Heidolph rotary evaporator and associated equipment
- J.T. Baker anhydrous sodium sulfate, granular 12-60 mesh or equivalent
- LC target analyte spiking solution, 400 ng/mL in EtOAc (see SOP "Air sampling with ASE cells" for preparation instructions)
- Organomation nitrogen evaporator system (N-evap)
- Pasteur pipettes and bulbs
- Personal protective equipment (gloves, safety glasses or goggles, and lab coat)
- Ring stands equipped with two-sided burette holders
- Scoopula
- SOP "Air sampling with ASE cells"
- SOP "Analytical methods for the determination of selected TO-4A pesticides by liquid chromatography tandem mass spectrometry (LC/MS/MS)"
- SOP "Extracting TO-4A air samples with the Dionex 300"
- SOP "Gas chromatography-mass spectrometry method for the analysis of TO-4A pesticides"
- Surrogate spiking solution, 400 ng/mL in EtOAc (see SOP "Extracting TO-4A air samples with the Dionex 300" for preparation instructions)
- TO-4A air sample extracts

7 Procedure

NOTE: It is important for all users to read the entire SOP before beginning any of the procedure and to ask questions if any of the instructions are unclear.

It is assumed that samples have been collected, extracted, and reduced to dryness prior to beginning these procedures. Previously extracted QA/QC samples, such as blanks, duplicates, and spikes will be cleaned up and analyzed along with the samples.

7.1 Sample and column sorbent preparation

1. Reconstitute the samples with 5 mL of hexane. Swirl flask to distribute the solvent to areas where compounds may be stuck to the glass.
2. Florisil and sodium sulfate must be stored in the laboratory at 120 °C for at least 24 h prior to use.

7.2 Column preparation

1. Remove the Florisil and sodium sulfate from the oven and allow them to cool to room temperature on a laboratory bench.
2. Place one chromatography column in the burette holder with the frit at the bottom for each sample. Insert the Teflon stopcock and tighten the retaining nut (see Figure E1. Florisil column setup. and Figure E2. Column packing.). Mark each column with a permanent marker to identify the corresponding sample.
3. Using a clean scoopula, fill each column with approximately 10 grams of Florisil. Gently tap each column to settle the Florisil (a permanent marker is a good instrument for tapping). Add 1-2 cm of anhydrous

sodium sulfate to the top of the Florisil (see Figure E2. Column packing.). Gently tap each column to settle the sodium sulfate.

4. Place a 100 or 150 mL beaker under each column.
5. Ensure that the stopcocks are in the closed position. Add 50 mL of hexane to each column prior to loading samples.
6. Turn the stopcocks to the open position and allow the hexane to drain through the column (flow rate unimportant) into the beakers until the level of the solvent is 1-2 cm from the top of the sodium sulfate.
7. Close the stopcocks until the samples are ready to load onto the column.
8. The collected hexane may be discarded in an appropriate waste container.

7.3 Eluant preparation

1. Prepare 6%, 15%, and 50% v/v mixtures of EtOAc in hexane, enough for the number of samples involved in the cleanup step.
2. Label six 125 mL flat-bottom flasks with ground glass stoppers for each sample (one for each of six fractions) with analyst's initials; sample identification information; fraction number; and, if desired, fraction composition.
3. Using Table E2. Solvent type and volume for six Florisil column eluants and a 50, 100, or 250 mL graduated cylinder, add the following volume of each solvent to the appropriately labeled flask for each sample.

Table E2. Solvent type and volume for six Florisil column eluants

Fraction no.	Solvent	Volume (mL)
1	Hexane	40
2	6% EtOAc in hexane	125
3	15% EtOAc in hexane	125
4	50% EtOAc in hexane	125
5	EtOAc	100
6	Acetone	100

4. Place a clean glass stopper in each flask.

7.4 Confirming Florisil elution pattern

NOTE: Prior to sample analysis for both GC and LC compounds on the same extracts, a decision must be made regarding two standards added to the samples. $^{13}C_3$ Atrazine and D_{10} Diazinon *cannot* be used simultaneously as a surrogate for GC compounds and as an internal standard for LC compounds. The addition of these compounds prior to extraction will impact the internal standard quantitation by LC. A suggested compromise is to select one of these compounds as a GC surrogate and the other as an LC internal standard.

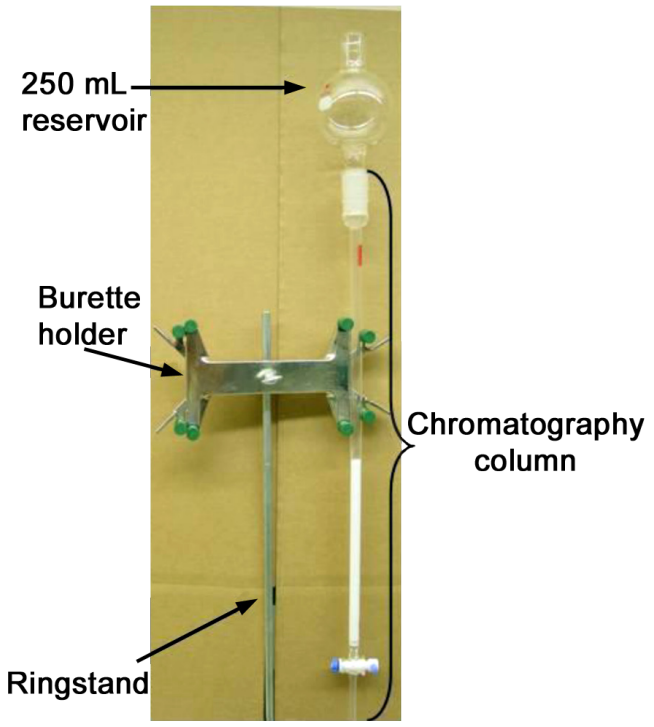

Figure E1. Florisil column setup.

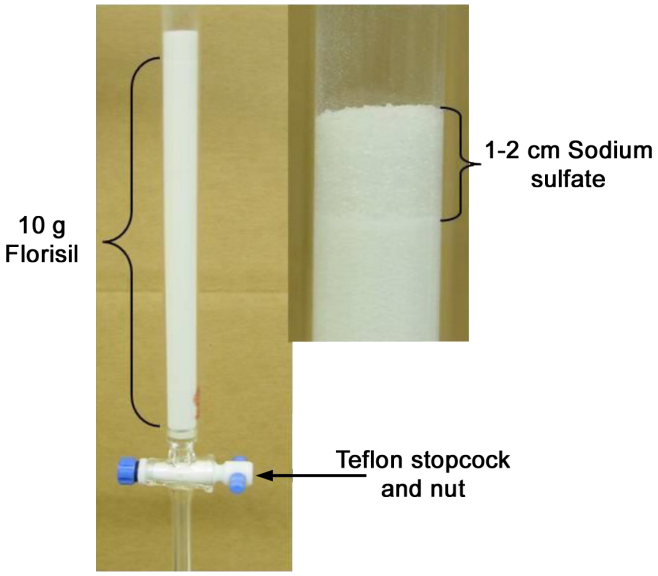

Figure E2. Column packing.

1. Because Florisil may vary from batch to batch and among different manufacturers, each new batch or lot of Florisil should be checked using this procedure to confirm the elution pattern of the compounds of interest.
2. Prepare one Florisil column as described in section 9.7.2.
3. Using an Eppendorf pipet, combine 1000 mL of surrogate spiking solution, GC target analyte spiking solution, and LC target analyte spiking solution (each 400 ng/mL in EtOAc) in a 150 mL beaker.
4. Evaporate the 3 mL of EtOAc to dryness using a nitrogen evaporator.
5. Reconstitute the sample with 5 mL of hexane.
6. Continue the sample cleanup steps described in section 9.7.5.
7. Split the sample fractions for LC and GC analysis as described in section 9.7.6, but *do not combine fractions* for GC analysis.
8. Analyze each fraction separately to determine which compounds elute in each fraction and that the collected fractions meet the method's needs. Details for sample analysis are described in SOP "Gas chromatography-mass spectrometry method for the analysis of TO-4A pesticides" and SOP "Analytical methods for the determination of selected TO-4A pesticides by liquid chromatography tandem mass spectrometry (LC/MS/MS)."
9. Record the percent recovery in table form in the laboratory notebook (fraction number and compound). Include the date of the pattern determination, brand, and lot number of the Florisil. Make sure that the compounds elute with >75% cumulative recovery in the fractions collected.

7.5 Sample cleanup

1. Open the stopcock on one column and allow the previously added hexane to drip out slowly into a beaker.
2. When the solvent level has reached the top of the Na_2SO_4, use a Pasteur pipette to load the sample (in 5 mL hexane) onto the appropriate column. Run the liquid down the side of the glass column to help insure that the Florisil bed is not disturbed during sample loading. The stopcock should remain slightly open during this procedure, with the solvent dripping into a beaker.
3. Add 5 mL of hexane to the sample flask and swirl to remove residues from the sides of the glass.
4. Wait until the solvent level has reached the top of the Na_2SO_4 before adding the rinse to the column with a Pasteur pipette.
5. Place the empty 250 mL reservoir on top of the column.
6. Pour the 40 mL hexane eluant from the Fraction 1 flask into the sample flask.
7. Remove the beaker from beneath the column and quickly replace it with the Fraction 1 flask to collect the first fraction.
8. When the solvent level has reached the top of the Na_2SO_4, pour the 40 mL of hexane eluant from the sample flask through the reservoir and onto the column.
9. Adjust the stopcock so that the drip rate is approximately one drip per second.
10. Repeat steps 1 through 9 for each sample. Be aware of the solvent level in each column and do not allow it to drop below the level of the top of the Na_2SO_4.
11. Pour the 125 mL eluant (6% EtOAc in hexane) from the Fraction 2 flask into the sample flask.
12. When the solvent level has reached the top of the Na_2SO_4, pour the 125 mL of 6% EtOAc in hexane eluant from the sample flask through the reservoir and onto the column.
13. Remove the flask labeled Fraction 1 and stopper this flask. Immediately place the labeled Fraction 2 flask under the column tip to collect the second fraction.
14. Repeat steps 11 through 13 for each sample.
15. Repeat steps 11 through 14 for each eluant fraction (see Table E2. Solvent type and volume for six Florisil column eluants for composition and volume).
16. When the last fraction has reached the top of the Na_2SO_4, open the stopcock fully to collect any remaining drips.
17. When no additional solvent drips off the column, remove the flask labeled Fraction 6 and stopper this flask.
18. Remove the Teflon stopcock and reservoir.
19. After allowing the columns to dry at least overnight, remove the Florisil and Na_2SO_4 by dumping them out the top of the column into a beaker. A dust gun or other source of dry air may be required to eliminate all of the solids from the column. The Florisil and Na_2SO_4 mixture should be disposed in an appropriate solid waste container.

7.6 Sample splitting

1. Get clean 100 and 250 mL graduated cylinders, the sample fractions, hexane and acetone squirt bottles, and additional solvents for each fraction (see Table E2. Solvent type and volume for six Florisil column eluants).
2. Label two 500 mL flat-bottom flasks with ground glass stoppers for each sample (not for each fraction) with the analyst's initials, sample identification information, fraction number (1 through 3 and 4 through 6 for GC analysis), and fraction composition.

3. Split Fraction 1.
   a. Pour Fraction 1 into the 100 mL graduated cylinder.
   b. Add hexane to the cylinder until the total volume is easily divisible by two (on a line). Record this volume in the laboratory notebook.
   c. Pour Fraction 1 back into the flask for mixing purposes.
   d. Pour half of the volume into the 100 mL graduated cylinder. Stopper the flask containing the remaining LC portion of the fraction.
   e. Empty the graduated cylinder into the 500 mL flask labeled for GC Fractions 1 through 3.
   f. Rinse the 100 mL graduated cylinder once with acetone, then hexane. Discard the rinsate.
4. Split Fraction 2.
   a. Pour Fraction 2 into the 250 mL graduated cylinder.
   b. Add 6% EtOAc in hexane to the cylinder until the total volume is easily divisible by four (on a line). Record this volume in the laboratory notebook.
   c. Pour Fraction 2 back into the flask for mixing purposes.
   d. Pour half of the volume into the 250 mL graduated cylinder. Stopper the flask containing the remaining LC portion of the fraction.
   e. Empty the graduated cylinder into the 500 mL flask labeled for GC Fractions 1 through 3.
   f. Rinse the 250 mL graduated cylinder once with acetone, then hexane. Discard the rinsate.
5. Split Fraction 3.
   a. Pour Fraction 3 into the 250 mL graduated cylinder.
   b. Add 15% EtOAc in hexane to the cylinder until the total volume is easily divisible by four. Record this volume in the laboratory notebook.
   c. Pour Fraction 3 back into the flask for mixing purposes.
   d. Pour half of the volume into the 250 mL graduated cylinder. Stopper the flask containing the remaining LC portion of the fraction.
   e. Empty the graduated cylinder into the 500 mL flask labeled for GC Fractions 1 through 3.
   f. Rinse the 250 mL graduated cylinder once with acetone, then hexane. Discard the rinsate.
6. Split Fraction 4.
   a. Pour Fraction 4 into the 250 mL graduated cylinder.
   b. Add 50% EtOAc in hexane to the cylinder until the total volume is easily divisible by four. Record this volume in the laboratory notebook.
   c. Pour Fraction 4 back into the flask for mixing purposes.
   d. Pour half of the volume into the 250 mL graduated cylinder. Stopper the flask containing the remaining LC portion of the fraction.
   e. Empty the graduated cylinder into the 500 mL flask labeled for GC Fractions 4 through 6.
   f. Rinse the 500 mL graduated cylinder once with acetone, then hexane. Discard the rinsate.
7. Split Fraction 5.
   a. Pour Fraction 5 into the 100 mL graduated cylinder.
   b. Add EtOAc to the cylinder until the total volume is easily divisible by two. Record this volume in the laboratory notebook.
   c. Pour Fraction 5 back into the flask for mixing purposes.
   d. Pour half of the volume into the 100 mL graduated cylinder. Stopper the flask containing the remaining LC portion of the fraction.
   e. Empty the graduated cylinder into the 500 mL flask labeled for GC Fractions 4 through 6.
   f. Rinse the 100 mL graduated cylinder once with acetone, then hexane. Discard the rinsate.
8. Split Fraction 6.
   a. Pour Fraction 6 into the 100 mL graduated cylinder.
   b. Add acetone to the cylinder until the total volume is easily divisible by two. Record this volume in the laboratory notebook.
   c. Pour Fraction 6 back into the flask for mixing purposes.
   d. Pour half of the volume into the 100 mL graduated cylinder. Stopper the flask containing the remaining LC portion of the fraction.
   e. Empty the graduated cylinder into the 500 mL flask labeled for GC Fractions 4 through 6.
   f. Rinse the 100 mL graduated cylinder once with acetone, then hexane. Discard the rinsate.
9. **Repeat** steps 3 through 8 for each sample. Between samples, rinse each graduated cylinder with an additional portion of acetone and hexane to reduce the possibility of cross-contamination.
10. After splitting, Florisil column fractions are evaporated to dryness using a rotary evaporator. Dryness is obtained when the condenser is no longer dripping solvent. **NOTE**: The rotary evaporator water bath temperature should not exceed 40 °C.
11. Stopper the sample flasks and store at room temperature until instrumental analysis. If the instrumental analysis will not begin within 1 week, the stoppered sample flasks should be refrigerated.

8 Data and Records Management

Data and records management issues are discussed throughout the procedure. Data will be recorded promptly, legibly, and in permanent ink in the logbook and in laboratory notebooks designated for each instrument and project. Electronic data files related to the project should be specified in the laboratory notebook.

9 Quality Control and Quality Assurance

QA/QC is discussed throughout this document, but additional parameters are listed below. All samples, including QA/QC samples, are treated in the same way as environmental samples throughout this procedure. Because Florisil may vary from batch to batch and among different manufacturers, the elution pattern of the compounds of interest should be checked as described in section 9.7.4 for each batch or lot of Florisil. Surrogate standards are employed for the GC compounds that will be monitored for acceptable method performance.

10 Waste Management

Solid, liquid, and glass waste are disposed of in separate containers. Solvents and solids used in this procedure should be disposed according to health and safety regulations and with appropriate labeling and record keeping. Several compounds used in this method (aldrin, dieldrin, heptachlor, and methyl parathion) are to be disposed of separately with "P" coded waste.

11 References

SOP "Air sampling with ASE cells"

SOP "Extracting TO-4A air samples with the Dionex 300"

SOP "Gas chromatography-mass spectrometry method for the analysis of TO-4A pesticides"

SOP "Analytical methods for the determination of selected TO-4A pesticides by liquid chromatography tandem mass spectrometry (LC/MS/MS)"

Appendix F
Standard Operating Procedure: Gas Chromatography-Mass Spectrometry Method for the Analysis of TO-4A Pesticides

1 Method Summary

This SOP describes the analysis of selected TO-4A pesticides by electron impact GC/MS in selected ion mode. A DB5-type chromatography column is utilized for the separation portion of the analysis. Once separated, the analytes are ionized in the mass spectrometer where fragments specific to each compound are detected. Three internal standards (tetrachloro-*m*-xylene [TCmX], $^{13}C_6$ d-HCH, and decachlorobiphenyl [DCBP]) are used to minimize small differences in instrumental conditions during analysis. Additionally, up to four GC surrogate standards (^{13}C atrazine, D_{10} diazinon, D_{10} chlorpyrifos, and heptachlor epoxide A) are analyzed to quantify and correct for extraction efficiency. The calibration range for this method is 50-300 pg/mL.

2 Scope and Application

This SOP is part of an effort to update the TO-4A method, "Determination of pesticides and PCBs in ambient air using high volume PUF sampling followed by gas chromatographic/multi-detector detection." Updates include stainless steel sampling cartridges that can be extracted by an automated accelerated solvent extractor (ASE), XAD-2 resin sorption bed, and mass spectrometry. This SOP updates TO-4A from multidetector detection for GC amenable compounds (high vapor pressure) to one detection technique, mass spectrometry. This improvement results in a more sensitive and selective method. All analytes, surrogates, and internal standards for this method are listed in Table E2. Solvent type and volume for six Florisil column eluants.

This SOP assumes the following.

- The instrument has been properly installed according to the manufacturer's specifications; accessories and attachments have been installed and verified as functioning correctly; and it is in its operational location and ready for general use.
- An autosampler is used with this system.
- The operator has access to the manufacturer's instrument, accessory operating, software, and reference manuals and current laboratory SOPs; see Equipment and Supplies.
- The operator is trained and knowledgeable in the use of a GC system.
- Internal standard calibration
- The samples to be analyzed by this method have been collected, extracted, cleaned up, and reduced to dryness prior to final determination.

Table F1. Target analytes, surrogate compounds, and internal standards for this method

Target analytes			
Alachlor[2]	Aldrin[2]	Atrazine[1]	Captan[3]
cis-Chlordane[3]	*trans*-Chlordane[3]	Chlorothalonil[2]	Chlorpyrifos[2]
2,4-D ethyl ester[1]	2,4-D methyl ester[1]	Dacthol[2]	*p,p'*-DDE[3]
o,p'-DDT[3]	*p,p'*-DDT[3]	Diazinon[2]	Dicloran (Botran)[1]
Dieldrin[3]	Ethyl parathion[2]	Fenchlorphos (Ronnel)[2]	Folpet[3]
a-HCH[1]	b-HCH[1]	Heptachlor[2]	Heptachlor epoxide B[3]
Hexachlorobenzene[1]	Lindane (g-HCH)[2]	Malathion[2]	Methyl parathion[2]
Methoxychlor[3]	Metolachlor[2]	Mirex[3]	*trans*-Nonachlor[3]
Oxychlordane[3]	Propazine[1]	Simazine[1]	Trifluralin[1]
Surrogate standard compounds			
^{13}C Atrazine[1]	D_{10} Chlorpyrifos[2]	D_{10} Diazinon[2]	Heptachlor epoxide A[3]
Internal standard compounds			
TCmX[1]	$^{13}C_6$ d-HCH[2]	DCBP[3]	

[1]Target analytes and surrogates using TCmX as an internal standard
[2]Target analytes and surrogates using $^{13}C_6$ d-HCH as an internal standard
[3]Target analytes and surrogates using DCBP as an internal standard

3 Personnel Qualifications

This SOP is written for users who have experience keeping a laboratory notebook and operating a gas chromatographic mass spectrometer and is trained in and can use Microsoft Excel. The operator should have a background in science with laboratory experience and must be trained by experienced personnel before undertaking these techniques. The operator must be able to understand the information in operating manuals and the SOPs related to this procedure.

4 Health and Safety

Standard laboratory protective clothing is required at all times during chemical operations in accordance with a health and safety research protocol. Operations involving the handling of solvents should be performed under a fume hood. The toxicity or carcinogencity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard, as most are pesticides. The following compounds are on the "P" list should be handled only in a fume hood with proper personal protective equipment: aldrin, dieldrin, heptachlor, and methyl parathion. "P" coded (acutely toxic) and PCB waste (DCBP) also must be disposed of separately. Please check with laboratory or safety personnel on proper disposal of these compounds.

When running a sample using the autosampler or when troubleshooting the autosampler, keep hands away from the syringe needle to avoid puncture wounds. The needle is sharp and may contain hazardous chemicals. The Agilent 6890 is supplied with a three-conductor power cord that provides a protective grounding when plugged in to a properly wired receptacle. Proper receptacle grounding must be verified. Wear safety glasses to prevent possible eye injury from flying particles while handling, cutting, or installing glass or fused-silica capillary columns. Observe caution in handling capillary columns to prevent skin puncture wounds. Many parts of this instrument are kept at a high temperature (>100 °C), including the injector, transfer line, and oven. Use extreme caution when touching these zones and allow them to cool or wear heat resistant gloves when performing maintenance.

5 Definitions, Acronyms, and Abbreviations

µg	microgram
µL	microliter
µm	micrometer
cm	centimeter
DCBP	decachlorobiphenyl (PCB 209)
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
GC/MS	gas chromatographic mass spectrometry
HCH	hexachlorocyclohexane
HP	Hewlett-Packard
ID	inner diameter
m	meter
m/z	mass to charge ratio
min	minute
mL	milliliter
mm	millimeter
msec	millisecond
ng	nanogram
PCB	polychlorinated biphenyl
pg	picogram
psi	pounds per square inch
PUF	polyurethane foam
QA/QC	quality assurance/quality control
RSD	relative standard deviation
s	second
SIM	selected ion monitoring
SOP	standard operating procedure
TCmX	tetrachloro-*meta*-xylene

6 Equipment and Supplies

- 100 µg/mL stock solutions of 36 target analytes, 4 surrogate standards, and 3 internal standards (see Table E2. Solvent type and volume for six Florisil column eluants)
- 100-1000 mL Eppendorf pipet and tips
- –20 °C freezer
- 25 mL volumetric flask and stopper
- Autosampler vials and caps
- Helium (99.9999%) research grade with gas purifier
- Hewlett-Packard or Agilent GC/MS system with autosampler—with all accessories and in working condition
- High-purity ethyl acetate
- Laboratory notebook
- Personal protective equipment (gloves, safety glasses or goggles, and lab coat)
- TO-4A samples
- Varian VF5-MS with 10 m easy guard (0.25mm ID, 0.25 µm film thickness, 30 m length) or similar DB5 type column

7 Procedure

NOTE: It is important for all users to read the entire SOP before beginning any of the procedure and to ask questions if any of the instructions are unclear.

7.1 Sample preparation

It is assumed that samples have been collected, extracted, cleaned up, and reduced to dryness prior to beginning these procedures.

1. Prepare fresh GC internal standard solution for all GC internal standards in ethyl acetate (150 pg/mL each TCmX, $^{13}C_6$ d-HCH, and DCBP). This can be accomplished for a variety of final volumes, but the suggested method follows.

a. If individual internal standard solutions are available, remove them from freezer storage and allow them to reach room temperature. Otherwise, prepare a 3 µg/mL solution of each individual internal standard by diluting 300 mL of 100 µg/mL stock standard to 10 mL with ethyl acetate.

- Prepare a 150 pg/mL solution of all three internal standards by diluting 1.25 mL of each 3 µg/mL solution to 25 mL with ethyl acetate.

2. Label standards with the solution name, concentration, solvent, date made, expiration date (6 months from date made), and preparers initials.
3. Pipet 1 mL of the 150 pg/mL internal standard solution into each sample flask.
4. Stopper and swirl the flask to remove any residues that might be sticking to the sides.
5. Remove the stopper and pipet the solution into a labeled autosampler vial and cap it.
6. Repeat steps 4 through 6 until all samples have been transferred to autosampler vials.

7.2 Calibration standard preparation

NOTE: Prior to sample analysis for both GC and LC compounds on the same extracts, a decision must be made regarding two standards added to the samples. $^{13}C_3$ Atrazine and D_{10} Diazinon *cannot* be used simultaneously as a surrogate for GC compounds and as an internal standard for LC compounds. The addition of these compounds prior to extraction will impact the internal standard quantitation by LC. A suggested compromise is to select one of these compounds as a GC surrogate and the other as an LC internal standard.

1. If calibration standard solutions are available, remove them from freezer storage and allow them to reach room temperature.
2. Otherwise, prepare six calibration standard solutions containing 36 target analytes, 4 surrogate standards, and 3 internal standards using Table E2. Solvent type and volume for six Florisil column eluants. See Table E2. Solvent type and volume for six Florisil column eluants for the identity of these compounds. These standards cover a concentration range of 50-300 pg/mL. This procedure assumes that all stock solutions have a 100 µg/mL concentration, and the final volume of the calibration solutions is 25 mL in each case.
3. Label standards with the solution name, concentration, solvent, date made, expiration date (6 months from date made), and preparer's initials.
4. After each standard is prepared or equilibrated, pipet at least 1 mL of each into a separate labeled autosampler vial. Include the standard's name, concentration, date prepared, and preparer's initials on the label.

7.3 GC/MS instrument setup

General operation and maintenance of the GC/MS system are not detailed here. The user will follow their laboratory's SOP for GC/MS analysis and manufacturer's recommendations using the specific instrument parameters for this analysis detailed below.

Initial GC/MS setup

- Ensure that the instrument is not leaking and is tuned.
- Ensure that the two rinse vials are filled with ethyl acetate and the two waste vials are empty.

Table F2. Preparation of calibration standards

Standard #	Compound type	Volume of stock (mL)	Final Concentration (ng/mL or pg/mL)
1	Target analytes	12.5	50
	Surrogate standards	12.5	50
	Internal standards	37.5	150
2	Target analytes	25	100
	Surrogate standards	25	100
	Internal standards	37.5	150
3	Target analytes	37.5	150
	Surrogate standards	37.5	150
	Internal standards	37.5	150
4	Target analytes	50	200
	Surrogate standards	50	200
	Internal standards	37.5	150
5	Target analytes	62.5	250
	Surrogate standards	62.5	250
	Internal standards	37.5	150
6	Target analytes	75	300
	Surrogate standards	75	300
	Internal standards	37.5	150

- Use a Varian VF5-MS with 10 m easy guard (0.25 mm ID, 0.25 µm film thickness, 30 m length) or similar DB5 type column.
- Either create and save or load the acquisition method for this analysis. GC/MS method parameters are listed below.

GC parameters

- Max oven temp 350 °C
- Equilibration time ³ 0.5 min

GC Temperature program

- Initial temperature 50 °C hold 2 min
- Ramp 1 15 °C/min to 150 °C hold 0 min
- Ramp 2 5 °C/min to 280 °C hold 0 min
- Ramp 3 15 °C/min to 300 °C hold 5 min
- Total time 41 min

Injection parameters

- Injection: One sample wash; three sample pumps; 2-mL injection; no Solvent A rinses; three Solvent B rinses; Viscosity Delay 0; Plunger speed fast
- Injector temp 230 °C
- Injector pressure 18.69-psi helium in constant pressure mode; 1.6 mL/min; 40 cm/s

MS parameters

- Electron impact ionization mode
- Quad temp 150 °C
- Source temp 230 °C
- Multiplier offset 400, Absolute mode off
- Solvent delay 8 min
- Selected ion monitoring—see Table E2. Solvent type and volume for six Florisil column eluants for ion windows
- Transfer line temp 300 °C

NOTE: Prior to sample analysis, the MS windows must be verified. Analyze a standard solution containing all 36 target analytes, 4 surrogate compounds, and 3 internal standard compounds in scan mode. Ensure that the retention times of the compounds and mass spectral windows are correlated to properly capture the eluting peaks. Slight adjustments may be needed after instrument maintenance or column clipping.

7.4 GC/MS calibration

General operation and calibration of the GC/MS system are not detailed here. The user will follow their laboratory's SOP for calibration and quantitation utilizing the specific instrument parameters for this analysis detailed below.

1. The internal standard/analyte pairs are listed in Table E2. Solvent type and volume for six Florisil column eluants by superscript. Be sure to set up the calibration compound list so that the correct internal standard will be used for each analyte and surrogate compound. Calibration curves must have an R^2 value greater than 0.90.
2. When preparing to analyze the samples and calibration standards, alternate them throughout the sequence to capture any instrument drift in time. Because the instrument is calibrated for each sample set, daily and continuing calibration standards are not necessary, but also may be included throughout the sample sequence.

Table F3. Instrumental selected ion monitoring parameters and ion windows

Group/start time (min)	Compound	Retention time (min)	Target *m/z*	Qualifier *m/z*	Backup *m/z*	Dwell time (ms)
1/8.0	Tetrachloro-*m*-xylene	13.630	207	209	244/242	75
	2,4-D methyl ester	13.851	199	234	175	75
2/14.0	Trifluralin	14.251	306	264	290	100
3/14.45	2,4-D ethyl ester	14.872	175	248		40
	a-HCH[1]	15.005	183	109	181/219	40
	Hexachlorobenzene	15.094	284	286	249	40
4/15.25	Dicloran (Botran)	15.449	206	208		40
	Simazine	15.649	201	186		40
	Atrazine	15.793	200	215		40
	^{13}C Atrazine	15.793	203	218		40
	b-HCH[1]	15.871	183	181		40
	Propazine	15.904	214	229		40
	Lindane (g-HCH)[1]	16.115	183	109		40
5/16.25	D_{10} Diazinon	16.296	183	314		75
	Diazinon	16.426	179	137		75
	Chlorothalonil	16.692	266	264		75
6/16.85	$^{13}C_6$ d-HCH	17.092	187	189		40
	Methyl parathion	18.301	263	125		40
	Alachlor	18.312	160	188		40
	Heptachlor	18.534	272	274		40
	Fenchlorphos (Ronnel)	18.656	285	287	125	40

Group/start time (min)	Compound	Retention time (min)	Target *m/z*	Qualifier *m/z*	Backup *m/z*	Dwell time (ms)
7/19.0	Malathion	19.511	127	125		40
	D_{10} Chlorpyrifos	19.577	324	99		40
	Metolachlor	19.633	162	238		40
	Chlorpyrifos	19.721	314	97		40
	Aldrin	19.777	263	265		40
	Dacthol	19.899	301	299		40
	Ethyl parathion	20.021	291	139		40
8/20.6	Oxychlordane	21.175	185	387		45
	Heptachlor epoxide B[2]	21.197	353	81		45
	Heptachlor epoxide A[2]	21.342	353	81		45
	Captan	21.590	79	149		45
	Folpet	21.798	260	262		45
	trans-Chlordane[3]	22.041	373	375		45
9/22.25	*cis*-Chlordane[3]	22.496	373	375	237	80
	trans-Nonachlor	22.596	409	407	237	80
10/22.95	*p,p'*-DDE	23.339	246	248	318	5
	Dieldrin	23.483	263	277	79	75
11/23.9	*o,p'*-DDT[4]	24.925	235	237	165	100
	p,p'-DDT[4]	26.196	235	237	165	100
12/27.0	Methoxychlor	28.221	227	228	152	100
13/29.0	Mirex	29.842	272	274	237	100
14/31.5	DCBP	33.825	498	500	214	100

[1,2,3,4]Compounds share fragmentation pattern.

3. Be sure to recap and archive the autosampler vials in a –20 °C freezer after they have been analyzed.

7.5 GC/MS quantitation

NOTE: TO-4A samples that have been split for GC and LC analysis will have a concentration twice that calculated. Be sure to add a correction factor before reporting results.

Sample calculation QC

Verify that calculations are correct by manually deriving the answer for a portion of the data based on the following criteria.

- Verifier will not be involved in data generation.
- Ten percent of mathematical calculations are checked.
- Calculations to be checked are randomly determined.
- Initial or sign and date calculations that were verified.

8 Data and Records Management

Data and records management issues are discussed throughout the procedure. Data will be recorded promptly, legibly, and in permanent ink in the logbook and in laboratory notebooks designated for each instrument and project. Electronic data files related to the project should be specified in the laboratory notebook. Electronic instrument data must be stored in duplicate at separate locations. This will be accomplished within 4 weeks of data collection or file creation. Compiled data may be printed and attached to laboratory notebooks with tape so long as a line is drawn through the attached page and onto the notebook page with initials and date.

9 Quality Control and Quality Assurance

QA/QC is discussed throughout this document, but additional parameters are listed below. Compare ongoing data quality checks with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. At a minimum, one sampling blank (with air, no spiking solutions), one sample duplicate (with air, no spiking solutions), and one QA spike (no air, GC and LC spiking solutions added) are included for each sampling event and should be analyzed together.

- Blank samples should not contain residues at a level higher than the lowest calibration standard.
- Replicate samples should agree within ±20%.
- QA spike samples should have a recovery between 75% and 120%.
- Surrogate compounds should have a recovery between 75% and 120%.
- If any of these requirements are not met, related samples should be flagged as having QA measures outside of acceptable limits. Corrective actions for future samples should be investigated.
- Calibration curves must have an R^2 value greater than 0.90.

In addition to quantitative measures of comparison, analysts should evaluate chromatograms and instrument operation. Questions that should be asked include the following.

- Are peaks symmetrical? Broad peaks and excessive tailing may indicate a leaky septum, a dirty injection liner, or a dirty column. Also, the column fittings may need to be tightened.
- Is the response obtained comparable to the response from previous calibrations? Responses (area counts or peak height) should be within ±20% of previous analyses.
- Are nontarget peaks present in calibration standard chromatograms? If so, this may indicate breakdown of one or more standards. A new set of calibration standards should be made.
- Are interferences present in the blanks? This may indicate lab or solvent contamination. New standards and blanks should be prepared using fresh solvents. Additional research may be required to determine the source of interferences and eliminate them.
- Immediately correct any significant peak tailing, leaks, changes in detector response, and laboratory contamination.
- Recalibrate the instrument when the performance changes to the point that the calibration verification acceptance criteria cannot be achieved. In addition, significant maintenance activities or hardware changes also require recalibration. Tuning the GC/MS also requires recalibration.
- If the RSD of the response factors is less than or equal to 20% over the calibration range, then linearity through the origin may be assumed, and the average calibration or response factor may be used to determine sample concentrations.

10 Waste Management

Solid, liquid, and glass waste are disposed of in separate containers. Solvents and solids used in this procedure should be disposed according to health and safety regulations and with appropriate labeling and record keeping. Several compounds used in this method (aldrin, dieldrin, heptachlor, and methyl parathion, DCBP) are to be disposed of separately with “P” coded waste or PCB waste.

11 References

Agilent Technologies. Overview of the MSD Productivity ChemStation, 2003.

Agilent Technologies. Agilent ChemStation, Understanding

Your ChemStation, Part #G2070-91115, June 2003.

Appendix G

Standard Operating Procedure: Analytical Methods for the Determination of Selected TO-4A Pesticides by Liquid Chromatography-Tandem Mass Spectrometry (LC/MS/MS)

1 Method Summary

In this procedure, sample analysis is performed via LC/MS/MS operated with the turbo ion spray/atmospheric pressure ionization (API) source. Positive ionization is used for all pesticides listed in the method. Transition ion pairs and retention times are used to verify the identities of analytes. Isotopically labeled internal and surrogate standards are used for quantitation and quality control. This method is valid for samples containing between 50 and 250 ng of each analyte.

2 Scope and Application

Although the SOP is somewhat specific to a particular EPA research situation, it can easily be used as a starting point for further development outside its original use. This SOP describes the method for detection and quantification of selected pesticides by liquid chromatography/tandem mass spectrometry (LC/MS/MS) using target transition ions to determine the presence of analytes in the sample extracts. The relevant pesticides are listed in Table E2. Solvent type and volume for six Florisil column eluants. The SOP is applicable to samples collected on XAD-2 media that has been pre-cleaned under the relevant NERL SOP.

This SOP assumes the following.

- The instrument has been properly installed according to the manufacturer's specifications; accessories and attachments have been installed and verified as functioning correctly; and it is in its operational location and ready for general use.
- An autosampler is used with this system.
- The operator has access to the manufacturer's instrument, accessory operating, software, and reference manuals and current laboratory SOPs; see Section 12.6
- The operator is trained and knowledgeable in the use of a LC system.
- Internal standard calibration
- The samples to be analyzed by this method have been collected, extracted, cleaned up, and reduced to dryness prior to final determination.

3 Personnel Qualifications

This SOP is written for users who have experience operating a liquid chromatograph-tandem mass spectrometer (LC/MS/MS) and a rotary evaporator, and are trained in keeping a laboratory notebook and the use of Microsoft Excel. The operator should have a background in science with laboratory experience, must be trained by experienced personnel before undertaking these techniques, and have completed the required laboratory safety training. The operator must be able to understand the information in the operating manuals and SOPs related to this procedure.

4 Health and Safety

Standard laboratory protective clothing, gloves, and eye covering is required when performing chemical operations, such as aliquoting standard solutions into autosampler vials for analysis and recapping standard solutions and sample extracts vials after analysis for storage.

Table G1. LC target analytes and internal standards

LC target analytes			
Allethrin[d]	Atrazine[a]	Bendiocarb[a]	Carbaryl[a]
Carbofuran[a]	Chlortoluron[a]	Cinerin I[d] & II[b]	Diazinon[b]
Diuron[a]	Dicrotophos[a]	Fenvalerate[d]	Fluometuron[a]
Jasmolin I[d] & II[b]	Linuron[a]	Monuron[a]	*cis*-Permethrin[c]
trans-Permethrin[d]	Propazine[a]	Propoxur (Baygon)[a]	Pyrethrin I[d] &II[b]
Resmethrin[d]	Simazine[a]	Tebuthiuron[a]	
LC internal standard compounds			
$^{13}C_3$ Atrazine	D_{10} Diazinon	$^{13}C_6$ *cis*-permethrin	$^{13}C_6$ *trans*-permethrin

[a]Target analytes using $^{13}C_3$ Atrazine as an internal standard
[b]Target analytes using D_{10} Diazinon as an internal standard
[c]Target analytes using $^{13}C_6$ *cis*-Permethrin as an internal standard
[d]Target analytes using $^{13}C_6$ *trans*-Permethrin as an internal standard

5 Definitions, Acronyms, and Abbreviations

Extract: The sample extract that contains native target analytes, surrogate recovery standard, and internal standard

Surrogate Recovery Standard (SRS): The compound used for QA/QC purposes to assess the extraction efficiency obtained for individual samples. The concentration of the SRS is determined by the expected concentration of the pesticide in each tissue sample. The SRS is spiked into the sample prior to extraction and quantified at the time of analysis. The SRS recovery indicates the extraction and recovery efficiency. Acceptable recovery of the SRS is 100% ± 20%. If recovery of the SRS is outside of the acceptable limits, the sample tissue is reanalyzed. The SRS standard(s) to be used for all analysis will be determined by the chemist performing the analysis.

Internal Standard (IS): The compound is added to sample extracts prior to LC/MS/MS analysis. The ratio of the instrument response from the analyte relative to the response from the corresponding IS is compared to ratios obtained for calibration curve solutions, where the IS level is fixed and the analyte levels varied. The IS is used to correct for minor run-to-run differences in LC injection, chromatographic behavior, and MS ionization efficiency. The IS to be used for all analysis is determined by its ionization mode and its retention time relative to the analyte of interest (see Table E2. Solvent type and volume for six Florisil column eluants). The included internal standards are $^{13}C_6$ *cis*-permethrin, $^{13}C_6$ *trans*-permethrin, D_{10} diazinon, and $^{13}C_6$ atrazine.

Acquisition Method: Under Analyst Software, the LC/MS/MS conditions used to analyze one or more samples

Acquisition Batch: Under Analyst Software, a group name assigned to a set of vials in the autosampler tray so that all samples may be analyzed in order under conditions specified in the method

Quantitation Method: Under Analyst Software, the method used to define the integration parameters for a set of samples. This method also defines ion pairs that are IS(s) and assigns analytes to the appropriate IS.

µL	microliter
CE	collision energy
CXP	collision excitation potential
DP	declustering potential
HPLC	high-performance liquid chromatography
LC/MS/MS	liquid chromatograph/mass spectrometer/ mass spectrometer
min	minute
mM	millimolar
mm	millimeter
SOP	standard operating procedure
T_r	retention time
V	volt

Quantitation Wizard: Under Analyst Software, the method used to define whether a sample is a standard, blank, unknown, or quality control. Also used to assign concentrations to the standards so that concentrations of the unknown samples may be calculated.

6 Equipment and Supplies

- Agilent 1100 high-pressure liquid chromatography system coupled with an Applied Biosystems API 4000 triple quadrupole mass spectrometer
- PC with Analyst Software and printer
- Analytical Column—Zorbax C18, 150 × 3 mm
- 5 mM ammonium acetate in water
- Methanol (pesticide grade or better)

7 Procedures

LC/MS/MS analysis

General operation and maintenance of the LC/MS/MS system are not detailed here. The user will follow their laboratory's SOP for LC/MS/MS and manufacturer's recommendations using the specific instrument parameters for this analysis detailed below.

7.1 Initial LC/MS/MS setup

The column is installed in the LC separations module and the mobile phase flow rate is set.

LC Parameters

- Mobile-phase program: 5 mM ammonium acetate in water (A) and 100% MeOH (B)
- Preinjection equilibration: 5 min @ 10% A: 90% B
- Mobile-phase ramp: 7 min to 4% A: 96% B
- Final mobile phase: 1 min @ 4% A: 96% B
- Column flow rate: 400 µL/min
- Total run time: 8 min
- Column oven temp: 30 °C
- Injection volume: 2.0 µL

MS/MS Parameters

- Positive ion mode
- Run time: 8 min
- Column flow rate: 400 µL/min
- Curtain gas setting: 40
- GS1 setting: 40
- GS2 setting: 407
- IS voltage: 5500
- Temperature: 400 °C
- Mass spectrometer source: electrospray, positive ion mode
- Exit potential: 10 V
- Collision cell gas setting: 2

Table G2. Analyte-specific LC/MS/MS parameters

Compound	T_r (min)	DP	CE	CXP	Transition ions
Allethrin	3.62	66.0	15.0	8.0	303.24/135.31
Fenvalerate	4.80	51.0	23.0	12.0	437.17/167.24
cis-Permethrin	6.89	46.0	25.0	12.0	408.14/183.24
trans-Permethrin	5.94	46.0	25.0	12.0	408.14/183.24
Resmethrin	5.83	41.0	59.0	8.0	356.16/128.17
Pyrethrin I	4.42	66.0	13.0	10.0	329.24/161.35
Pyrethrin II	2.85	36.0	19.0	10.0	390.21/161.41
Jasmolin I	5.35	66.0	15.0	10.0	331.24/163.53
Jasmolin II	3.28	71.0	15.0	10.0	375.21/163.40
Cinerin I	4.45	66.0	25.0	6.0	317.24/107.13
Cinerin II	2.86	71.0	31.0	6.0	361.18/107.16
Bendiocarb	1.82	61.0	13.0	6.0	224.24/109.09
Carbaryl	1.88	31.0	17.0	8.0	219.26/145.04
Propoxur (Baygon)	1.83	51.0	19.0	6.0	210.27/111.06
Carbofuran	1.84	61.0	29.0	10.0	222.23/165.31
Diazinon	2.71	71.0	31.0	10.0	305.17/169.27
Dichrotophos	1.65	61.0	17.0	6.0	238.20/112.02
Chlorotoluron	2.01	66.0	37.0	4.0	213.22/71.85
Diuron	2.01	61.0	35.0	12.0	233.16/71.82
Fluometuron	1.89	66.0	41.0	4.0	233.16/71.82
Linuron	2.21	61.0	25.0	10.0	249.13/160.09
Monuron	1.89	61.0	27.0	12.0	199.20/71.84
Tebuthiuron	1.98	61.0	25.0	10.0	229.23/172.20
Simazine	1.97	66.0	27.0	8.0	202.20/132.01
Propazine	2.26	76.0	31.0	10.0	230.21/146.00
Atrazine	2.09	71.0	25.0	10.0	216.27/174.05
$^{13}C_6$ *cis*-Permethrin	6.88	46.0	23.0	12.0	414.15/189.40
$^{13}C_6$ *trans*-Permethrin	5.92	46.0	23.0	12.0	414.15/189.40
D_{10} Diazinon	2.67	76.0	31.0	10.0	315.21/154.23
$^{13}C_3$ Atrazine	2.09	71.0	25.0	12.0	219.27/177.02

- Compound-specific parameters: see Table G2. Analyte-specific LC/MS/MS parameters

7.2 LC/MS/MS internal standard calibration

1. Area counts for each analyte are determined automatically using the Analyst software provided with the API 4000. Each chromatogram is reviewed by the operator to insure proper and consistent integration, and manual correction of inappropriate integrations is performed if necessary.
2. A calibration curve for each analyte will be constructed with a minimum of five concentrations that encompass the relevant calibration range. The internal standards are present at equal concentrations in all samples and standards. Details regarding the specifics of each standard, including actual concentration, will be recorded in the appropriate laboratory notebook.
3. The calibration curve will be generated using the theoretical analyte concentration versus the relative area (analyte area/IS area). The calibration curve may not be forced through the origin. The coefficient of determination (R^2) of the curves must be ≥0.99.

7.3 LC/MS/MS analysis sequence

1. A solvent blank is analyzed first to verify that the LC/MS/MS system is clean of carry-over or artifacts. The acceptance criterion is an analyte quantitation ion area that is two times lower than the area of the lowest level standard in the previous set.

2. Five calibration standards are analyzed, followed by up to five sample extracts.
3. A mid-level calibration standard (from the calibration curve standards) is analyzed, followed by a blank.
4. The sample extract, mid-level standard, blank sequence is repeated until all samples in a set have been analyzed. After the final sample has been run, the complete set of calibration standards will be rerun. In this way, the calibration curve of standards reflects the condition of the instrument while samples are being analyzed. The percent relative error for recalculation of each calibration standard (including the mid-level control standard) against the initial curve must be <25%.

7.4 LC/MS/MS data processing

NOTE: TO-4A samples that have been split for GC and LC analysis will have a concentration twice that calculated. Be sure to add a correction factor before reporting results.

1. A calibration curve will be generated for each analyte and its respective internal standard from the results of the standard analyses. Each data file will be reviewed to ensure that the identification and integration of quantified target peaks are correct.
2. Analyte identification will be based on a retention time of ±0.2 min relative to the retention time of the two standards that bracket the sample in the LC/MS/MS run order.
3. The instrument software will calculate concentration of the analytes and surrogates in the sample based on the calibration curve. A quantitation report will be generated for each sample or standard.

7.5 Extract storage

Extracts are stored protected from light at –20 °C except during analysis.

8 Data and Records Management

- All operations, and instrument settings are electronically stored in the instrument's Analyst software on the computer used to control the LC/MS/MS.
- All original analytical results are located in specific study folders identified as projects. For any sample set, all files (acquisition, quantitation, etc.) associated with that sample set will have identical names except for the file extension. In addition to other descriptors, all file names will include the actual date of sample analysis.
- All compiled data will be reviewed by the analyst. For each analysis set, the calibration curve, results, and analytical sequence will be copied into an excel spreadsheet to include the following information.
  - Data ID/sample type
  - Notebook number and pages
  - Date extracted
  - Analyst name
  - Calibration standards concentration
  - Surrogate standards concentration
  - Internal standards concentration
  - Spike concentration
  - Comments
  - Sample list and location of each sample in autosampler tray
- All data files (to include Analyst files and Excel spreadsheets) are stored on disks for permanent record. The disks are stored permanently in the LC/MS/MS laboratory computer as part of the LC/MS/MS laboratory records. Periodically, these files will be copied and backed up to an additional storage media. This backup will maintain the integrity of the file structure.
- Final calculations of the data are performed and/or recorded in the study database and are a responsibility of the analyst.

9 Quality Control and Quality Assurance

- The absolute response levels for the internal standard will be recorded for each analysis. If IS areas decrease throughout a sample set or if a difference is observed in the area of the IS in samples and in standards, but the SRS recoveries in samples remain within the acceptance range, then no action will be taken. If IS areas decrease or if a difference is observed in the area of the IS in samples and in standards, and the SRS recoveries in samples do not remain within the acceptance range, then corrective action will be taken. These actions will include cleaning the LC/MS/MS source, cleaning/replacing the ion probe capillary, changing the HPLC precolumn, cleaning the HPLC column, and/or repreparing the mobile phase and reanalyzing the a subset of the samples or the entire sample set.
- Samples will be reanalyzed when the calibration curve data cannot be fit to a first-order equation with fit parameter $R^2 > 0.99$ or when the recalculation of the standards against the curve does not meet the tolerances set in sections and . Corrective action, as listed in this section, will be undertaken before samples are reanalyzed.
- Surrogate recovery values of 70% to 130% in the actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than the minimum goal, the data will be flagged. For recoveries greater than the maximum goal, the concentration of the surrogate spiking solution will be checked against a calibration curve to determine whether inadvertent solvent loss has resulted in higher spike levels.

10 Waste Management

Solid, liquid, and glass waste are disposed of in separate containers. Solvents and solids used in this procedure should be disposed according to health and safety regulations and with appropriate labeling and record keeping.

11 References

Not applicable.

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