EXPEDITED FIELD SURVEY & SAMPLING TECHNIQUES FOR POLYCHLORINATED BIPHENYL (PCB) CONGENERS AND DIOXINS

Glen P. Jackson, Mengliang Zhang, Jen Bowman, Natalie Kruse, Dina Lopez

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FINAL REPORT: EXPEDITED FIELD SURVEY & SAMPLING TECHNIQUES FOR POLYCHLORINATED BIPHENYL (PCB) CONGENERS AND DIOXINS.

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Dec 14, 2012

ABSTRACT: This procedure describes a method for the on-site field analysis of polychlorinated biphenyls (PCBs) in soil samples. The method describes how a measured mass of soil sample is first treated with a mixture of potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4) before extraction of the PCBs using headspace SPME at elevated temperature (90°C). The extracted PCBs are then desorbed from the SPME fiber into the inlet of a portable GC-TMS system equipped with low thermal mass (LTM) GC column. The resulting chromatographic and mass spectrometry data is manually interpreted to determine the presences of Aroclors or PCB congeners. The total sample preparation and analysis time is less than 45 minutes.

Strengths:

- Allows on-site PCB determinations in soil
- Small samples required (10 g)
- <45 minute total analysis time (Including sample preparation, 30 minute SPME extraction and 6.5 minute GC-TMS separation/detection)
- Allows Aroclor determination
- Mass spectrometric identification of peaks/compounds
- Semi-quantitative
- Detection limits of ~10 ppm Aroclor 1260.
- No organic solvents required
- SPME sampling fiber is reusable for ~50 samples
- Method can be modified for other classes of pollutants, including TCE

Weaknesses:

- Not suitable for the ppb range of Aroclors in soil
- Method requires the use of acidic and oxidative reagents ($KMnO_4$ + H_2SO_4) to modify soil chemistry
    - Generates acid waste
- Accurate quantitation requires that the soil moisture content be known
- Torion GC-TMS not very well suited for semi-volatiles like PCBS
    - Instrument requires operation beyond intended temperature zones
    - Instrument requires dismantling and cleaning every 50-100 samples
- Instrument has shown stability and ruggedness problems, but improvements are continually being made
- Detection limits may limit potential applications
- Data requires manual interpretation
- SPME extraction step requires portable heater (with generator)
    - Torion is currently developing a portable SPME extraction oven
- Method is not suitable for dioxins due to their poor extraction recovery and low volatility
- PCB congener analysis not possible with current instrument performance

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1.0 INTRODUCTION

This method may be used for the rapid analysis and on-site detection of polychlorinated biphenyls (PCBs) in soil samples, either as Aroclors or as individual PCB congeners, using a portable gas chromatography-toroidal ion trap mass spectrometer (GC-TMS) system. The Aroclors and PCBs listed below have been determined by this method. The seven Aroclors listed below are commonly specified in US Environmental Protection Agency (EPA) regulations. The method also may be modified for use with other matrices such as tissue and aqueous samples, if appropriate sample extraction procedures are employed. This method has NOT been fully validated, but preliminary field tests demonstrated that Aroclor analyses with detection limits on the order of 10 ppm in soil are possible in a total analysis time of ~35 minutes.

Table 1. List of common Aroclors.

Compound	CAS Registry No.
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

Aroclors are multi-component mixtures, which contain different relative quantities of 209 possible PCB congeners. This procedure is used to rapidly determine selected groups of PCB congeners as Aroclor patterns for the observation and identification of Aroclors so that informed decisions can be made as quickly as possible. NOT all 209 PCB congeners can be separated using this method. This method may be used to determine the existence of Aroclors, some PCB congeners, or "total PCBs," depending on regulatory requirements and project needs, and additional approaches with greater quantitative accuracy should be applied if assessment purposes of the project include quantitative analysis of Aroclor or PCB congeners (refer to EPA Method 8082A[1] and EPA Method 1668B[2]). The determination of Aroclors is based on the observation of characteristic peak patterns in the resulting GC-TMS chromatograms. The Aroclors usually have been weathered by long exposure in the environment, which may make significant difference in

peak patterns compared to those of Aroclor standards. When samples contain more than one Aroclor, the species of Aroclors may not be able to be identified by using this method.

The analyst should select gas chromatography (GC) columns, solid phase microextraction (SPME) fibers suitable for target Aroclors. Examples are provided below. The stability of the analytical system must be established and the method or techniques employed must be appropriate for the analytes of interest in the analytical matrix of interest and at the levels of concern.

Prior to employing this method, it is recommended to consult the EPA method for each type of procedure that may be employed in the overall analysis (e.g. Methods 3500, 3600, and 8000) for additional information on quality control procedures, calculations, and general guidance.

Use of this method is restricted to use by, or under the supervision of, personnel appropriately experienced and trained in the use of portable GC-TMS and skilled in the interpretation of gas chromatograms and mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

A measured mass of dry or wet soil sample is treated with potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4) solutions and extracted using headspace SPME. The extract is desorbed from the SPME fiber in the GC-inlet of a portable GC-TMS system equipped with low thermal mass (LTM) GC column. The resulting chromatographic and mass spectrometry data is manually used to determine the presences of Aroclors or PCB congeners. Results are semi-quantitative and depend mostly on the quality of externally generated calibration curves and the moisture content of the soil. PCB analyses are typically reported as g PCB (or Aroclors) per g of dry soil, so the analysis of wet soils will underestimate the concentration of PCBs.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware must be demonstrated to be free of interferences by analyzing method blanks. Refer to EPA Methods 3500, 3600, and 8000 for a discussion of interferences.

3.2 Interferences co-extracted from the samples will vary. Four groups of interference sources can pose problems in PCB determinations, as follows:

3.2.1 Contaminated solvents, reagents, or sample processing hardware.

3.2.2 Contaminated SPME fiber, GC carrier gas, parts, column surfaces, or detector surfaces.

3.2.3 Compounds extracted from the sample matrix and SPME vial septum.

3.2.4 Co-elution of related analytes -- All 209 PCB congeners cannot be separated using the GC columns and procedures described in this method. If the samples encompass other congeners, the analyst must either document the resolution of the congeners in question or establish procedures for reporting the results of co-eluting congeners that are appropriate for the intended application.

3.3 Cross-contamination can occur if the apparatus and materials are not clean. Disposable glass vials with caps are recommended for sample preparation and extraction. Otherwise, all glassware should be scrupulously cleaned as soon as possible.

4.0 SAFETY

Refer to EPA method 8082A and Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of chemicals listed in this method. Appropriate personal protective equipment (PPE) and hazardous waste handling should follow standard best practices.

5.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products is for illustrative purposes only. Common laboratory apparatus such as beakers and pipettes are not listed.

5.1 Portable GC-TMS

The Guardion 8 GC-TMS (Torion Technologies, American Fork, Utah, USA) consists of a low thermal mass GC and a miniature toroidal ion trap mass analyzer. The system uses a fast heating low thermal mass injector and a miniature vacuum system, which contains a miniature dual-stage diaphragm roughing pump and a miniature turbo-molecular pump. The instrument can be ready for an injection within 3 minutes of powering on. A 90-cm^3 disposable helium cartridge and a rechargeable battery (Figure 1) provide the carrier gas and electric power to the GC-TMS system, respectively, which enable the portable stand-alone instrument to be used in the field without any other load. The entire system weighs about 13 kg (28 lb) and is 47 cm × 36 cm × 18 cm (18.5 × 14 × 7 in.) (Figure 1). The

instrument can be operated from the on-board color touch LCD screen, or via a laptop connection. Commercially-available LTM GC columns from Supelco can be used. In these studies, the column was an MXT-5, 5 m × 0.1 mm ID capillary column chemically bonded with 5% diphenyl/95% dimethyl polysiloxane, 0.4 μm film thickness.

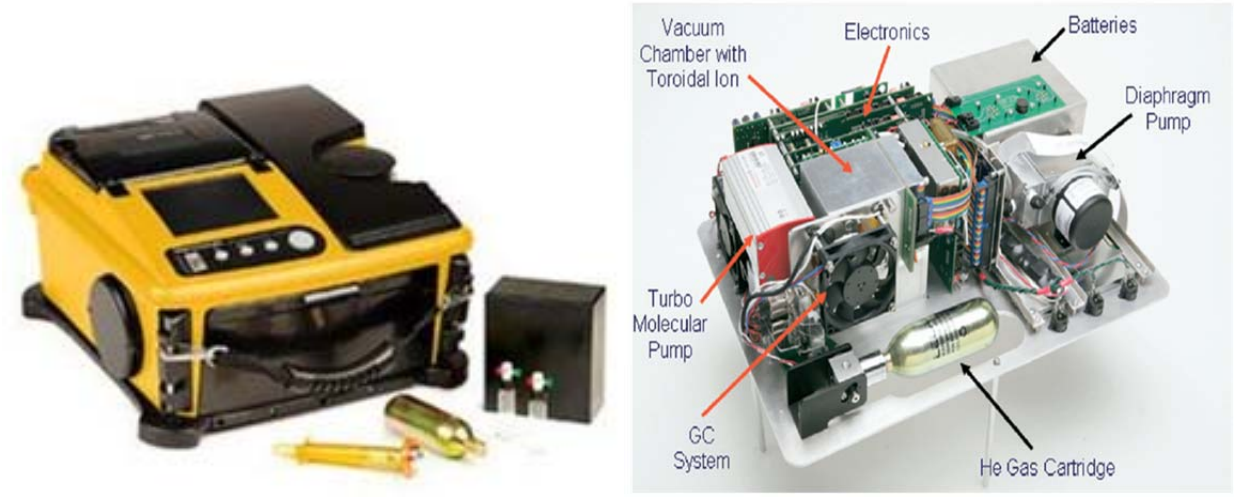

Figure 1. Photographs of the Guardion®-8 GC-TMS showing A) external and B) internal components.

5.2 SPME extraction

The SPME sampling device (Custodion®, Figure 2) provided by Torion is specially designed to be field-portable and easy to operate. The mechanism of the SPME holder is similar to automatic ballpoint pens. The SPME fiber can be extended out of or withdrawn into a protective metal needle just by pushing the plunger on top of the holder. Commercial SPME fibers from Supelco (Bellefonte, PA, USA) can be used in this holder. The types of the thin polymer-coated fibers should be selected according to the properties of target analytes. In these studies, as elsewhere, 100 μm PDMS fibers were found to be suitable for PCB analyses.

5.3 A portable balance capable of weighing to 0.01 g.

5.4 Sample vials and caps – 10 ml/20 ml glass headspace vials (SUN-SRI, Catalog No. 500 488/ Catalog No. 500 550) and crimp top caps (SUN-SRI, Catalog No. 500 272). Crimp pliers are also required.

5.5 A portable heating block/oven: capable of heating up to 100 °C within 30 minutes.

5.6 A stop watch or other timing device for monitoring sampling times.

5.7 A portable generator may be necessary to operate all the items for the SPME sampling.

Figure 2. Photograph of the Custodion® SPME sampling device provided by Torion.

6.0 REAGENTS AND STANDARDS

6.1 Chemicals used in all tests must be reagent-grade or pesticide-grade. Other grades may be used if it is ascertained that the purity of reagent does not lessen the accuracy of the determination. Reagents should be stored in glass containers to prevent the contaminants from plastic materials. Solutions/standards can be prepared in a laboratory setting and carried in appropriate secondary containers to the field site.

6.2 Standards used in this method include Aroclor 1016, 1221, 1232, 1242, 1248, 1254 and 1260. Other PCB standards may be needed for method development such as single PCB congener standards or EPA 8082A PCB standards, which contains 19 PCB congeners. Commercially prepared stock standards at any concentration can be used if they are certified by the manufacturer or by an independent source. Commercially available blank soil and PCB contaminated soil are recommended to simulate the real soil samples.

6.3 The following solvents may be necessary for the preparation of standards and extraction. All references to water in this method refer to organic-free reagent water (refer to EPA Methods 8000 for details).

6.3.1 Acetone, $(CH_3)_2CO$

6.3.2 Toluene, $C_6H_5CH_3$

6.3.3 Methanol, CH_3OH

6.3.4 Hexane, C_6H_{14}

6.3.5 Potassium permanganate, $KMnO_4$

6.3.6 Concentrated sulfuric acid, H_2SO_4

6.4 To enhance the extraction efficiencies from the soil samples and to overcome matrix effects (such as acidity, moisture content etc.) the soil should be treated with acidified potassium permanganate. A Solution of 6 M H_2SO_4 is prepared from a stock solution of 95% H_2SO_4. A solution of 0.2 M $KMnO_4$ is prepared from a primary solid sample. The stock standard solutions can be purchased as certified solutions and can be diluted to standard solutions at certain concentrations.

6.5 Blank soil is used to study the matrix effect and simulate the PCB contaminated soil samples.

e.g. To simulate 10 ppm Aroclor 1260 contaminated soil samples, measure 0.5 g blank soil into the 10 mL glass vial and spike with 50 µl of 100 ppm Aroclor 1260 standard solution. Mix the soil and Aroclor 1260 solution by vortexing for several minutes. Dry the soil sample in the hood at room temperature. It usually takes 20~90 minutes to dry the samples depending the solvent of standard solutions.

$$C_{soil} = \frac{100\frac{\mu g}{ml}\ Aroclor\ \times\ 50\ \mu l}{0.5\ g\ soil\ \times\ 1000 \mu l/ml} = \frac{10\frac{\mu g}{g} Aroclor}{soil} = 10\ ppm\ Aroclor/soil$$

NOTE: The order of addition of the soil and Aroclor 1260 standard solution was found to not affect the results.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

The soil samples are recommended to be stored under refrigeration in the dark and should be analyzed within 40 days of sampling. However PCBs are very stable in a variety of matrices and conditions and the holding time may be as long as a year.

8.0 PROCEDURE

8.1 Sample extraction

Two 0.5 g aliquots of each soil sample are measured into two 10 mL glass vials. One is used for GC-TMS analysis, and the other is used as a back up or for moisture analysis, if necessary. To extract PCBs from the soil samples, add 2.5 ml 0.2 M $KMnO_4$ and 0.25 ml 6 M

H_2SO_4 to the 10 ml vial. After sealing the vial and vortexing for 30 seconds, extract the samples using headspace SPME for 30 minutes at 100°C. Commercial SPME fibers with 100 µm film thickness of polydimethylsiloxane (PDMS) are the best choice of fiber for headspace SPME of PCBS, and especially Arocolor 1260 in which mid-chlorinated PCB congeners (penta-, hexa- and hepta-PCBs) are most abundant[3].

NOTE: 20 ml vials can also be used instead of 10 ml vials. Longer extraction times can significantly improve the extraction efficiency[3c] but for on-site analysis a shorter analysis time is more desirable

8.2 Instrumental analysis

For the Aroclor 1260 determination, the GC-TMS temperature was programed as follows: 50 °C (hold for 60 s), rate 1.5 °C/s to 290 °C (hold for 150 s). The whole program was complete in 380 s (< 7 minutes). The injector was maintained at 280 °C and SPME fiber desorption was performed in the injection port for 1 minute. A constant helium flow of 1.0 ml/min was used. The compounds were detected by full scan mode with a scan range *m/z* 50 to 500. The EI source for the TMS detector was operated at 70 eV.

8.3 Tuning and calibration

Tuning conditions for the portable GC-TMS should be performed at least daily or on every start-up using the Calion calibration mixture (from Torion). Instrument conditions such as EI filament current, voltage and ion target current may need to be modified to assist with the optimization and tuning.

8.4 Identification of Specific Aroclors

The identification of specific Aroclors is based on the GC peak patterns and relative mass spectra. EPA 8082A standards, which contain 19 specific PCBs can be used to predict the general retention time windows of PCB homologs in Aroclors. Overall, the heavier PCBs have larger retention indices, which result in longer retention times, although some exceptions exist (see Table 2 and Figure 3). On the other hand, the comparison of mass spectra with National Institute of Standards and Technology (NIST) database can be another important source of information for PCB homologs or Aroclor. Other databases may be used, such as a laboratory self-established compound library using PCB standards.

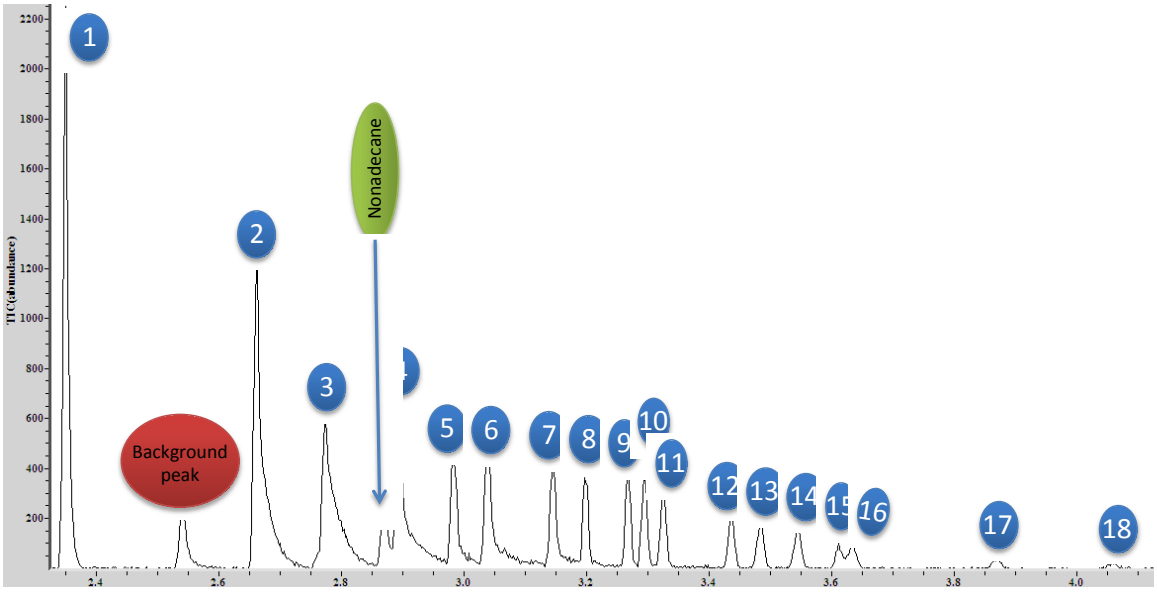

Figure 3. Example of headspace-SPME TIC of EPA 8082A standard (contains 19 PCB congeners) collected on the Torion Guardion®-8 GC-TMS, with nonadecane internal standard.

According to Table 3, the PCB distributions in different Aroclors are different and will therefore show characteristic peak patterns in resulting GC chromatograms. Light PCBs, which have a dominant proportion of 1~3 Cl substituents in their structures, are the major PCBs in Aroclor 1221, Aroclor 1016 and Aroclor 1232. Aroclors 1254 and 1260 contain relatively more chlorinated PCBs such as penta-, hexa- and hepta- chlorobiphenyls (CBs). Tri-CBs and tetra-CBs are found to be the most abundant PCBs in Aroclor 1242 and Aroclor 1248. To differentiate Aroclor 1016 and 1232, the relative amount between tri-CBs and tetra-CBs can be used. The tri-CBs are relatively more in Aroclor 1016. Similarly, to compare Aroclor 1242 and 1248, tri-CBs are more abundant in Aroclor 1242 but tetra-CBs are more in Aroclor 1248. The hepta- and octa- CBs can be used as characteristic patterns for Aroclor 1260. The differences between Aroclors 1016 and 1232, 1242 and 1248 are not very clear, so care must be taken when interpreting the results.

Table 2. Retention indices and mass information of 19 PCB congeners in EPA 8082A standards

	PCB Name	CAS	Retention Index	Molecular Mass and important fragment ions
1	2-Chlorobiphenyl	2051-60-7	1482	188, 190
2	2,3-Dichlorobiphenyl	16605-91-7	1695	222, 224
3	2,2',5-Trichlorobiphenyl	37680-65-2	1733	256, 258, 260
4	2,4',5-Trichlorobiphenyl	16606-02-3	1819	256, 258, 260
5	2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	1887	290, 292, 294
6	2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	1922	290, 292, 294
7	2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	2090	290, 292, 294
8	2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	2112	324, 326, 328
9	2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	2132	324, 326, 328
10	2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	2190	324, 326, 328
11	2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5	2157	358, 360, 362
12	2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	2328	358, 360, 362
13	2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	2332	358, 360, 362
14	2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	2355	358, 360, 362
15	2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	2343	394, 396
16	2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	2402	394, 396
17	2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	2439	394, 396
18	2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	2491	394, 396
19	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9	2721	464

Table 3. Comparison of PCB distributions in different Aroclors[4]

	Weight % in Aroclors						
Cl No.	1221	1016	1232	1242	1248	1254	1260
1	65.5		31.3				
2	29.7	21.2	23.7	14.7			
3	4.8	51.5	23.4	46.0	20.9	1.2	0.1
4		27.3	15.7	30.6	60.3	16.6	1.0
5			5.8	8.7	18.1	51.0	13.5
6					0.8	23.9	47.0
7						4.4	33.8
8						0.7	7.5
9							0.7
10							0.1

8.5 Quality assurance

8.5.1 Blanks

Before processing any samples, the analyst must demonstrate, through the analysis of a method blank, which all equipment and reagent interferences are under control. The blanks should be analyzed and verifiably blank before each set of samples is analyzed or each change in the method, including reagent and instrumental parameters.

The blanks should also be used after an analysis of concentrated sample to test if carryover exists. The carryover affects can be caused by insufficient desorption of SPME fiber or the contamination of GC-TMS system. If carryover is found, the SPME fiber should be re-desorbed and analyzed until sufficiently low carryover is determined.

8.5.2 Precision

The precision is assessed through replicate injections of different concentrations of Aroclor 1260. Precision for the peak areas for the extracted ion signals of selected PCBs is currently on the order of 20% RSD for the most abundant PCBs in Aroclor 1260. Precision is known to be improved through the use of internal standards, especially isotopically-enriched analogues.

8.5.3 Quality control

The method detection limit of this method is currently ~10 ppm for Aroclor 1260 in dry soil, as determined by measurements of spiked calibration soil samples around this range. The performance of the portable GC-TMS system is not as stable as typical bench-top instruments such as the Thermo PolarisQ GC-MS system, which was also used during

method development. The quality control (QC) samples at the concentration of 10 ppm (may vary depending on regulatory requirements and project needs) should be prepared and analyzed before each time a set of samples is analyzed and after every 4 samples (*in other EPA method it's recommended to include at least a QC sample after each group of 20 samples.*). If the QC samples are not detected, the set before the QC samples should be reanalyzed.

8.5.4 Matrix effect and absolute recovery

The soil matrix can significantly depress the extraction efficiency of headspace SPME of PCBs relative to no soil.[3c] The addition of chemical modifiers is known to enhance sample recoveries and minimize variability caused by matrix effects.

9.0 WASTE MANAGEMENT

According to the EPA, laboratory waste management practices should be conducted consistent with all applicable rules and regulations. The air, water, and land must be protected by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

This method generates solvent and chemical waste that must be disposed of in accordance with environmental regulations. An adequate means of waste handling and disposal must be arranged to avoid the accumulation of hazardous waste material.

10.0 BACKGROUND REVIEW

10.1. Background studies and preliminary work

As persistent organic pollutants (POPs), PCBs are very stable and resistant to degradation under natural condition[5]. For qualitative analyses of PCBs in the environment, one can attempt to identify the various congeners of PCBs in a sample and compare the distribution to PCBs from different primary or secondary sources, such as Aroclors, soils or sediments samples. Aroclor analyses are based on the assumption that no significant change of congener composition in the Aroclor has occurred under the environmental conditions. However, in some cases the individual congeners differ to varying extents from the original Aroclor sources. In one study, Du et al.[6] compared their data with Rushneck et al.[7] in an attempt to identify the source of PCBs in atmospheric samples. Of the comparison peaks, 10 of the 42 resolved peaks could not be matched with

the Rushneck data. Another, simpler qualification method is to identify the 19 PCB congener as the "markers" of different kinds of Aroclors. Many of these 19 congeners represent congeners specific to the common Aroclor formulations (see Table 2, for example). Aroclor-based methods are therefore prone to some uncertainty. Two important sources of variance in the EPA methodology are the subjective assignment of Aroclor speciation and RRFs[8] and the assumption that the enough stability in PCB congener compositions to determine probable source Aroclors.[9] As an example, the total PCBs based on marker congeners and peak ratios overestimated the concentrations determined by summing the concentrations of individual congeners by using COMSTAR algorithm.[10] This artifact occurs because the alteration of PCBs such as degradation in weathered samples was not counted in COMSTAR estimations.[11] Other efforts such as using normalized PCB concentrations in samples to those in Aroclor standards have been done,[12] but the concentrations found in weathered environmental samples can hardly be adequately represented.

For quantification of PCBs, two methods are currently used, Aroclor-based methods and congener-specific methods. The Aroclor-based methods include (i) the measurement of PCB peaks in the sample against the most similar Aroclor standard and (ii) the measurement of a small number of "marker" peaks, for which relative response factors (RRFs) have been determined, for each of several Aroclors. Congener-specific methods quantify all 209 resolvable individual congeners against PCB congener standards instead of Aroclor standards. Compared with congener-specific methods, Aroclor-based methods have high utility in identification of neat mixture and preliminary site screening,. Aroclor analysis has advantages such as lower cost, shorter analysis times and less burdensome requirements of advanced instrumentation

Congener-specific methods are becoming preferable because of the detailed PCB information offered. By providing concentrations of all the PCB congeners, the toxicity of each sample can be accurately estimated, even though the proportions of most toxic PCB congeners are considerably smaller than the major, less-toxic components of the Aroclors. The congener-specific method is recommended in carcinogenic risk-assessment.[13] On the other hand, the result of congener-specific method is not influenced by source and type of PCBs, the type of environmental media (air, water, soil, sediment, and biota), physical-chemical properties of the media (temperature, pH, organic carbon content), the congeners present in technical mixtures, or the type and abundance of microfauna and flora. Congener-specific methods can reflect physiological, spatial, and temporal changes that might not be tracked by Aroclor-based methods. The measurement of complicated samples, which combines of several Aroclors can also be achieved by using congener-specific methods.

Individual or full congener analysis is not likely to be possible in the proposed portable GC-TMS system presented here. The system employs only a singly, medium-resolution column and extensive sample cleanup prior to analysis is not realistic in the field. High-resolution chromatography and extensive sample preparation are both necessary for full congener-specific analysis.

10.1.1 Gas-chromatography-based methods

Both the Aroclor-based and the congener-specific methods of PCB analysis rely on gas chromatography.[14] Gas chromatography (GC) is a powerful analytical technique to separate individual PCB congeners or combinations of congeners based on their volatility (boiling point) and polarity. Open tubular capillary GC columns rather than older packed GC columns are now in common use because of their improved resolution, better selectivity, and increased sensitivity.

After GC separation, PCBs can be detected with electron capture detection (ECD), electrolytic conductivity detection (ELCD), or mass spectrometry (MS). Since the 1960s, PCBs have been detected by GC-ECD using packed columns. Capillary GC-ECD and capillary GC/MS have been in common use since the 1980s.[15] For GC/MS systems, PCBs are identified by order/time of elution from the GC, as well as through molecular and fragment mass to charge (m/z) ratios. High-resolution mass spectrometry (HRMS) techniques can be used to distinguish between certain coplanar PCBs, which are carcinogens at low level, but normally additional sample cleanup, special instrumentation and high-resolution mass spectrometer are required.

10.1.2 Typical detection limits

For Aroclor-based methods, method detection limits (MDLs) in the literature for Aroclors vary in the range of 0.054 to 0.9 mg/L in water and 57 to 70 ng/g in soils, with higher (worse) MDLs for the more heavily chlorinated Aroclors.

For congener-specific methods, MDLs of the GC-MS methods can be low to from parts per billion to parts per trillion.

10.1.3 Cost

Aroclor-based methods are relatively inexpensive in comparison to congener-specific methods. The cost on a per sample basis ranges from $50 to $500 for Aroclor-based methods, and from $500 to $2,000 for congener-specific methods depending on instrumentation used, the sample matrix, number of samples to be analyzed, and extent of quality-assurance-quality-control required.

10.1.4 EPA methods

EPA method 8082, which is an Aroclor-based method and EPA method 1668, which is a congener-specific method are both available. EPA method 8082 is an Aroclor pattern recognition and relies on GC-ECD instrumentation to analyze PCBs as Aroclors or as individual PCB congeners in extracts from solid or aqueous matrices.[1] As an Aroclor-based method, all 209 PCB congeners cannot be determined by this method. Another disadvantages of this method is that the use of decachlorobiphenyl (PCB 209) as an internal standard could result in negative bias if Aroclor 1268 is present in environmental samples because Aroclor 1268 contains 4.8% of PCB 209.[16] EPA Method 1668 (Revision A) is a congener-specific method used to measure individual PCB congeners in water, soil, sediment, and tissue by high resolution gas chromatography (HRGC)/high resolution mass spectrometry (HRMS).

10.2 Sample extraction and preparation methods

Both Aroclor-based and congener-specific methods are gas-chromatography methods, which require the extraction of PCB from the environmental matrix.

10.2.1 General introduction of PCB sample extraction methods

Many classical extraction techniques have been applied such as Soxhlet extraction,[17] liquid/liquid extraction (LLE),[17b, 18] solid-phase extraction (SPE),[19] and pressurized fluid extraction.[20] However, these methods have experienced some shortcomings that limit their application to high-throughput or on-site analysis. For example, Soxhlet extraction usually takes 16 to 24 hours and uses large volumes of solvent. Even though automatic Soxhlet extractors are available, about 2-hour extraction time is still needed.[21] LLE-based methods are laborious and also require large volumes of solvent. At the same time LLE is usually not as exhaustive as Soxhlet extraction and are often coupled with other extraction technics such as solid phase extraction (SPE).[22] SPE has been used as an alternative method to LLE for the extraction of PCBs from aqueous samples such as ground water and serum because of the smaller solvent consumption and shorter extraction time than LLE.[19b, c, 23] SPE has a few downsides such as clogging due to small particles and pore size of the sorbent in cartridges when directly performing extractions with complex-matrix samples such as soil and serum.[24] Pressurized fluid extraction requires the use of an expensive and large extraction device, which is inconvenient for on-site analysis.[20b, 25] All the methods above need to use large volumes of organic solvents, which is a major concern in light of green chemistry philosophies.[26]

Therefore, more extraction methods with high efficiency, short time and low cost have been developed in recent years such as vortex assisted liquid-liquid microextraction (VALLME),[18] dispersive liquid–liquid microextraction (DLLME),[27] hollow-fiber liquid-

phase microextraction (HF-LPME),[28] ultrasound assisted emulsification-microextraction (USAEME)[30] and solid-phase microextraction (SPME).[29] In VALLME, dispersion of the micro-volume level extraction solvent (organic phase) into the aqueous solution has been assisted by vortex mixing and it was able to take only 2 minutes to achieve equilibrium.[18] DLLME is very similar to VALLME but without vortex mixing. VALLME also requires an additional disperser solvent which can be miscible in both water and extraction solvent such as acetone, acetonitrile and/or methanol.[30] It has been reported that the combination of SPE and DLLME could achieve higher enrichment factor (EF) and was more suitable for the determination of PCBs even in complex matrices such as plant samples and milk.[27, 31] HF-LPME works based on the principle of supported liquid membrane.[26] First, a polypropylene membrane is immersed into the organic solvent several times to immobilize the solvent in the pores of the polymer. The extraction in the sample solution is then performed followed by filling the core of the hollow fiber with an acceptor solution. The organic solvent forms a thin layer within the wall of the HF to resist the aqueous solution into lumen. After the extraction, the acceptor solution can be injected to GC for analysis.[32] USAEME is another kind of liquid-liquid microextraction with the help of ultrasonic radiation. The ultrasound accelerates the mass-transfer process between two phases and facilitates the emulsification effects which short the extraction time and improve the extraction efficiency.[33]

SPME was first reported by Pawliszyn and co-workers in 1989,[34] and it has been greatly developed and widely applied over the past 20 years.[35] The thin polymer-coated fiber is the key part of the SPME devices. The fiber is placed in the sample or the sample headspace for the adsorption/absorption of analytes. After reaching equilibrium (ideally, but not always), the fiber is removed from the sample and the analytes are transferred from the fiber to a chromatographic column by either thermal desorption—in the hot GC injector or mobile phase—or through elution, as with high pressure liquid chromatography (HPLC).[35] SPME has some advantages compared with the traditional sample preparation technics such as LLE and SPE. First, it's a fast, simple, sensitive and solvent-free method. Second, SPME can integrate sampling, extraction, concentration and sample introduction to an instrument into one step. Third, it is compatible with major separation systems such as GC, HPLC and capillary electrophoresis.[36] Forth, commercialized fibers with various coating and combinations [e.g., PDMS, polyacrylate (PA), carboxen (CAR), carbowax (CW) and divinylbenzene (DVB)] are available and more fiber coatings such as polypyrrole (PPY),[37] poly(phthalazine ether sulfone ketone) (PPESK)[38] and polyurethane (PU)[39] foams have been developed. SPME is easy for automation and several instrument companies such as Thermo Scientific, Agilent have GC instruments with SPME autosamplers. Fifth, the device for SPME is small which is convenient for portable instrument and field/on-site analysis.

10.2.2 SPME phase selection

The mechanisms of SPME are adsorption and absorption and the relative proportion of each depends on the phase material and analytes. As the only manufacture, Supelco supplies SPME fibers with various single or mixed polymer materials.[40] For the liquid-coated fibers like PDMS, the analyte molecules can partition and penetrate the entire coating phase within a certain extraction time. For solid-coated fibers like polyacrylate, the analyte molecules are very difficult to diffuse into the coating phase because of the complex crystalline structures.[41] Therefore, absorption fibers have larger extraction volume which means a wider dynamic range but a longer time to reach equilibrium compared with adsorption fibers.[36] The interactions between analytes and the materials of fiber also follow the principle of 'like dissolve like'. For example PDMS (nonpolar) coating fiber provides high extraction efficiency for nonpolar compounds whereas PA (polar) coating fiber has more applications for polar compounds such as phenols and alcohols.[42]

Typically, SPME can be used in inserted mode or headspace mode. In inserted mode, the fiber is completely immersed in the liquid samples; in headspace mode, it is exposed to the vapor phase above the liquid or solid samples. For complex mixtures, headspace SPME is more preferable because it can protect the fiber from damage or carryover. Under headspace mode, the mass transportation of analytes from sample to headspace and then to fiber coating is easier for volatile compounds. So, headspace SPME typically works better for analytes of high-to-medium volatility and low-to-medium polarity.[43], The most important parameters for optimizing SPME method development include fiber coating, extraction mode, agitation method, sample volume, water/organic solvent composition, pH, extraction temperature, extraction time, ionic strength, desorption condition, and sometimes sample derivatization.

A study that used heated headspace SPME for the analysis of PCBS used a non-equilibrium 30 minute extraction to compare the sensitivity of the three fibers found the PDMS/DVB fiber to be much more sensitive for low-molecular-weight congeners, and the 100 μm PDMS fiber to be more sensitive for high-molecular-weight congeners than the other fibers.[3] Finally, 100 μm PDMS was chosen because it was the most efficient fiber for HS-SPME of target analytes under the selected experimental conditions.

In our project, for the qualification purpose, we used the simpler qualification method mentioned at the beginning of this review that identifies 19 PCB congeners as the markers to differentiate Aroclors. For this reason, 100 μm PDMS was used in these studies. However, several kinds of fibers are suggested to be investigated in the future, such as PDMS/DVB, 7 μm PDMS.

11.0 METHOD DEVELOPMENT

Aroclor 1260 was most frequently used for method development because of its relevance in the target application site (PORTS site). Significant work was accomplished to assess the general working range of the instrument, the necessary tuning and working conditions and general optimization. Much of this work was described in significant detail in the monthly report submitted throughout the active grant period.

11.1 Peak identities and general performance

A headspace SPME GC-TMS chromatogram of EPA 8082A standard containing 19 PCB Congeners was compared with a similar analysis of Aroclor 1260. The results are shown in Figure 4. Retention times and fragmentation pattern similarities between the EPA standard and the Aroclor standard enable peak assignments to be made in the Aroclor mix. As mentioned earlier, peak assignment is made with the knowledge that partial or complete co-elution of different PCB congeners cannot be excluded.

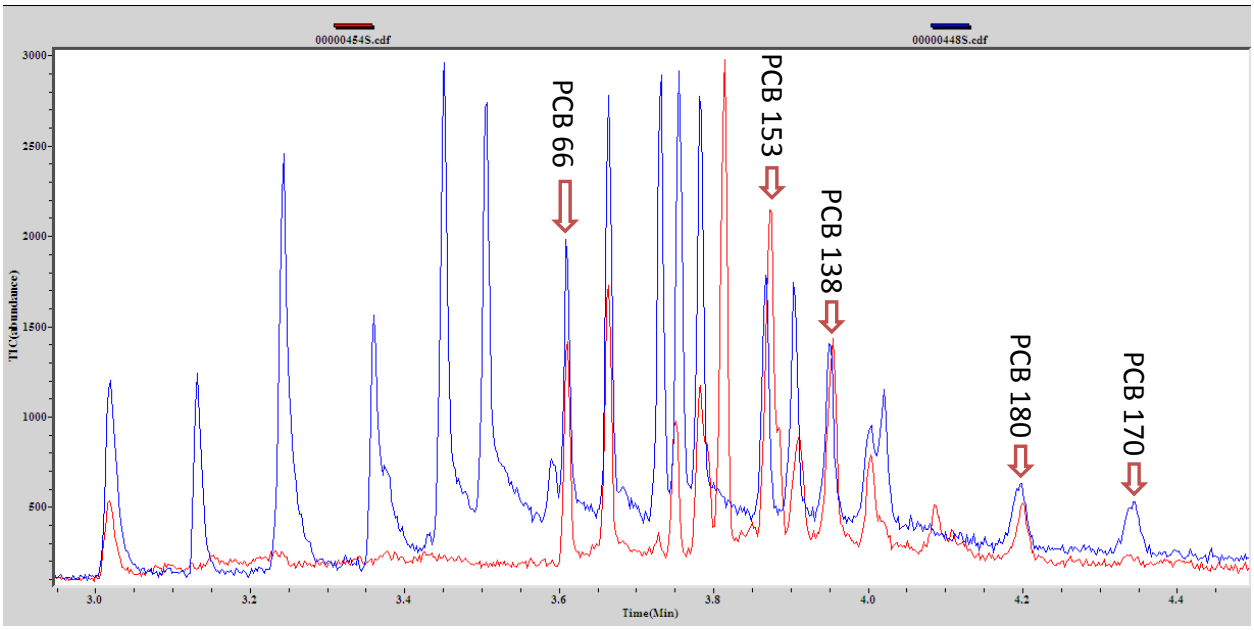

Figure 4. a) TIC of headspace SPME of 40 µL of 100 ppm Aroclor 1260 (red) and EPA 8082A mix (blue) on the Torion Guardion®-8 GC-TMS. Peak assignments for the Aroclor mix (red) cannot exclude the possibility of congener co-elution.

Although we cannot confirm that each peak is a unique PCB congener, the retention times and mass spectra of the difference peaks enable tentative assignments to be made for the most dominant congener present in each chromatographic peak. The tentative

assignments for several of the marked peaks in Figure 4 are PCB 66, 153, 138, 180 and 170. These peaks were used for quantitative analyses.

To identify different Aroclors, all the samples must be collected, extracted and detected in the same condition and system. Figure 5 (top) shows a Guardion® GC-TMS spectrum collected using this method. A comparison NIST spectrum for the expected PCB is also shown. The combination of retention time, fragment ion masses and isotope envelope all provide evidence for the peak assignment. Similar comparisons were completed for each tentatively assigned peak in the different Aroclor mixes.

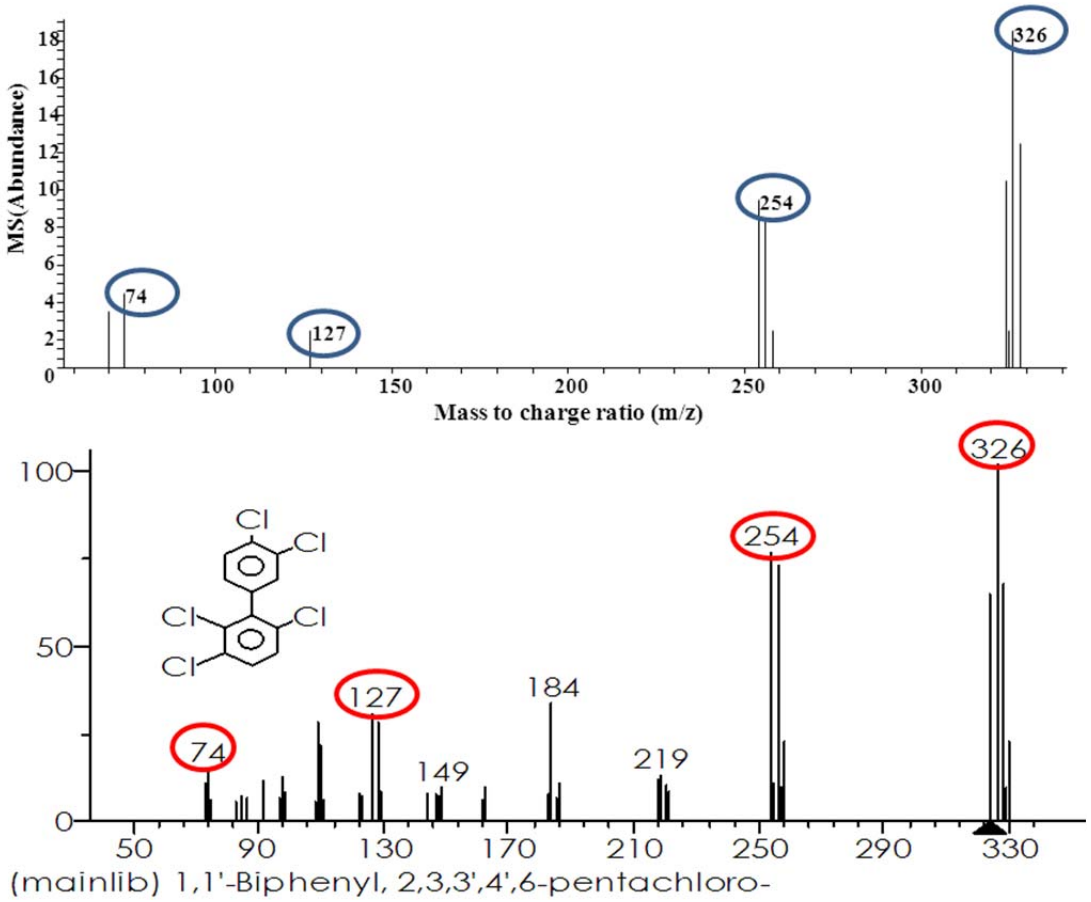

Figure 5. Example of mass spectra comparison for pentachlorobiphenyl between Torion Guardion®-8 GC-TMS data (top) with NIST database (bottom).

Calibration curves were collected on the Guardion 8® GC-TMS to assess the linearity of the response function near the limits of detection of the instrument. Aroclor 1260 standard solutions with different concentrations were prepared in empty glass vials (no soil, water or modifiers) and analyzed. Different volumes of 100 ppm Aroclor 1260 solution

were spiked into separate 10-ml vials. After the samples were dried in the hood under the room temperature, they were sealed and then extracted by SPME for 30 minutes under 100 °C. All the samples were analyzed using the same GC program on portable Guardion 8® GC-TMS. The result of different amounts Aroclor 1260 solutions was shown in Figure 6a. The total ion current (TIC) of 40 µl 100 ppm Aroclor 1260 solution in quadruplicates was shown in Figure 6b. From Figure 6b, it is clear that the reproducibility of the retention times and peak heights (or peak areas) of PCB congeners was not perfect; peak areas had percent relative standard deviations on the order of 20%.

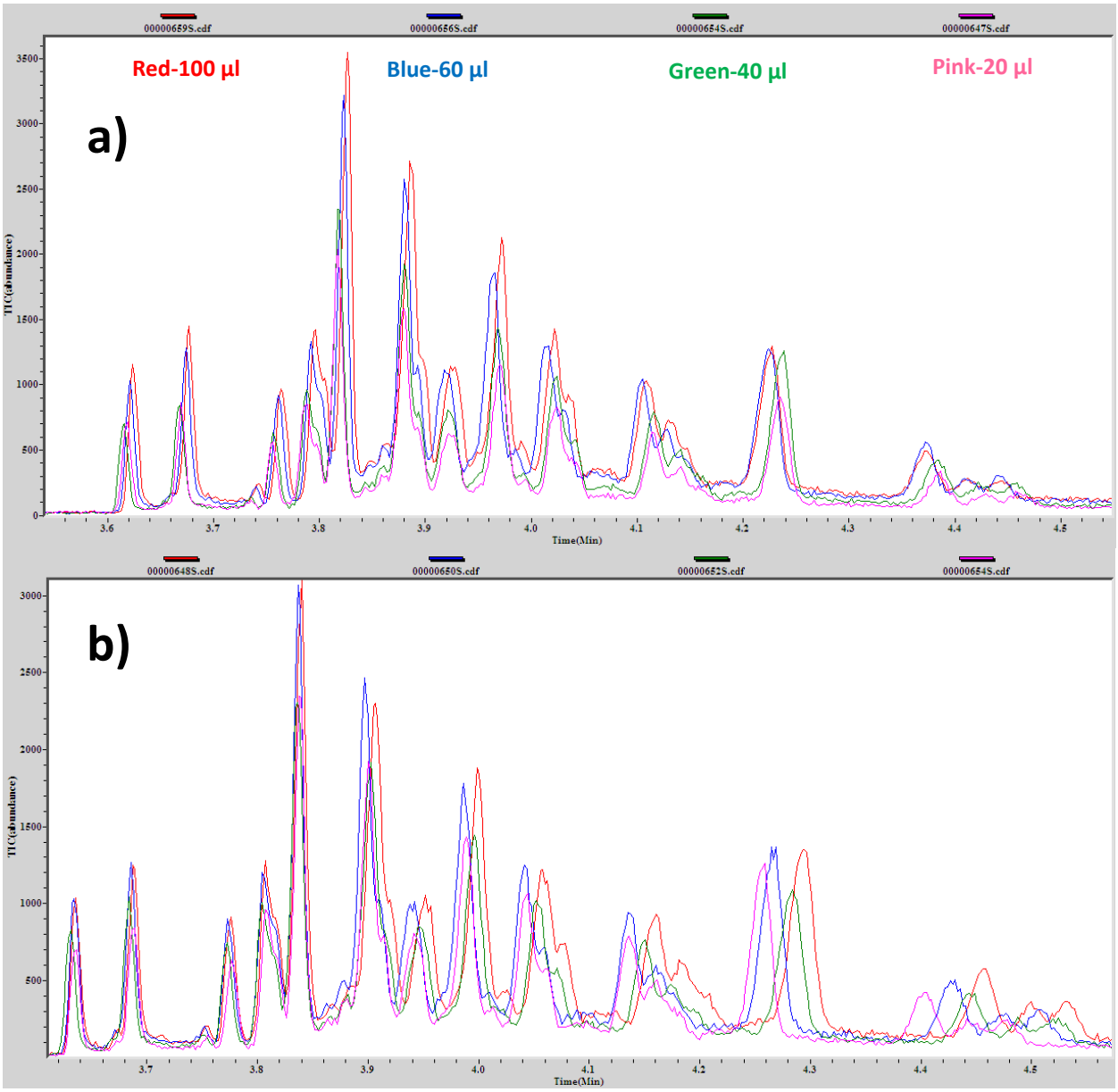

Figure 6. a) TIC of headspace SPME of different spike volumes of 100 ppm Aroclor 1260 standard solutions into an empty glass vial, b) Comparison of four replicate samples each at 40 µL spike level (4 µg Aroclor).

The results of the calibration curves collected on the Portable GC-TMS and bench-top GC-MS are shown in Figure 7. The five major PCBs identified in Figure 7 show linear relationships between the concentration and instrument response (peak height or area) on both instruments. However, the portable GC-TMS instrument had significantly higher (worse) detection limits and had poorer correlation values (expressed as R). Whereas the bench-top Polaris Q GC-MS consistently provided R values greater than 0.96, the portable

Torion GC-TMS gave weaker correlation scores, but still exceeding 0.94 (Note: Figure legend uses R^2 not R).

In general, these correlations are not acceptable for accurate quantitative purposes according to EPA method 8000.[44] In a certain concentration range, the peak area should be proportional to the total amount of material present, even if the peak shape or the baseline slightly changes. However, these calibration curves were conducted without the use of an internal standard, so the linearity and precision is expected to be superior to values presented here in a properly validated method.

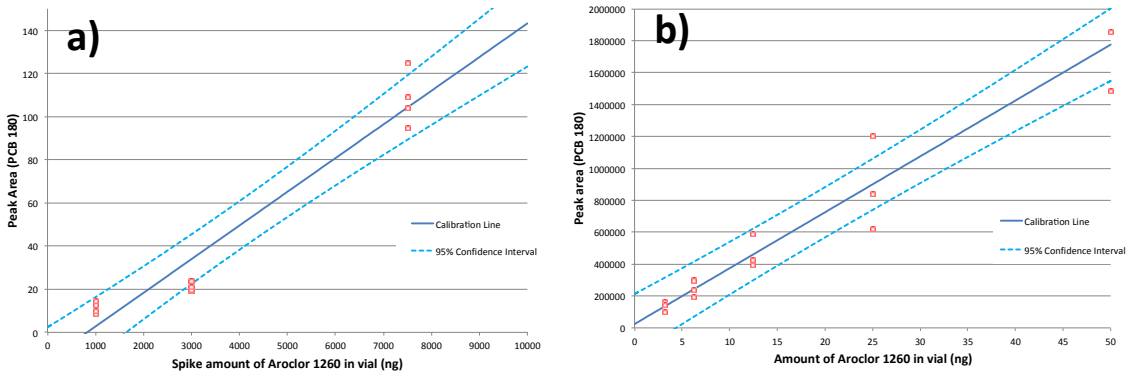

Figure 7. Comparisons of headspace SPME calibration curves of Aroclor 1260 for the peak tentatively assigned as PCB 180 collected on a) Portable Torion Guardion®-8 GC-TMS (R^2 = 0.93) and b) Bench-top Thermo Polaris Q GC-MS (R^2 = 0.94). Note that the bench-top calibration curve covers significantly lower quantities.

11.2 Affect of soil preparation

To investigate the effects of different soil sources and addition orders of soil and Aroclor 1260 standard solution for simulated soil samples, four groups of samples were prepared and analyzed using the portable GC-TMS system. For Group 1, 0.5 g dry blank soil (BK Soil) which is purchased from RT Corp, Laramie WY, US and 50 µl 100-ppm Aroclor 1260 isooctane standard solution were added into 10-ml vial. The vials were dried in the hood under room temperature for 1.5 hour. Group 2 was prepared in the same way except that the BK Soil was replaced by wet soil sample collected in December 2012 (Soil, GEL SAMPLE NO.: LBCRM2.4OU009B), which had been proven to contain PCBs lower than the minimum detectable quantity (sub ppb range). For Group 3, the 50 µl 100-ppm Aroclor 1260 isooctane standard solution was first added into the 10-ml vial and dried in the hood under room temperature for 1.5 h. Then the dry BK Soil was added into the vial and mixed. Group 4 was prepared in the same way as Group 3 except that the BK Soil was replaced by wet Soil (GEL SAMPLE NO.: LBCRM2.4OU009B).

After the spike and soils were mixed, 2.5 ml 0.2 M $KMnO_4$ and 0.25 ml 6 M H_2SO_4 were spiked into each vial. The samples were sealed and then extracted by SPME for 30 minutes at 100 °C. All the samples were analyzed using the 6.5 min GC program on the portable Torion Guardion® GC-TMS. Each group has four replicates. Three PCB peaks were chosen to compare the effects of different soil sources and addition orders of soil and Aroclor 1260 standard solution for simulated soil samples (Figure 8). The results are shown in Table 4. One-way analysis of variance (ANOVA) was performed on the resulting data (soils as factor, peaks as dependent variables) and no significant differences were found between the four groups (soil preparation methods) for any of the peaks. The ANOVA results support conclusion that the order of addition of the soil and Aroclor 1260 standard solution does not affect the subsequent headspace extraction results.

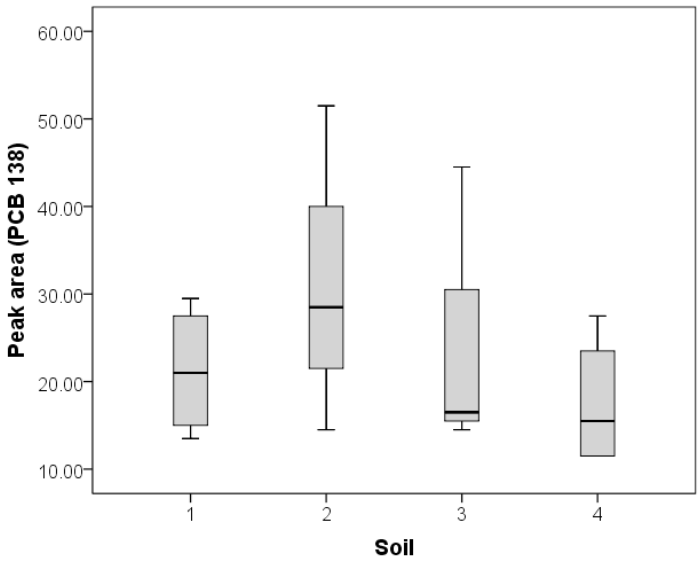

Figure 8. Box and whisker plot of the peak areas obtained for PCB 138 when soils for headspace SPME are prepared in different ways. Analyses performed on the Portable Torion Guardion® GC-TMS instrument.

Table 4. One-way analysis of variance (ANOVA) results using soils as factor and selected PCB peak areas as dependent variables. No significant differences were found between the four soil preparation methods.

		Sum of Squares	df	Mean Square	F	Sig.
PCB 153 * Soil	Between Groups	64.517	3	21.506	.097	.960
	Within Groups	2436.417	11	221.492		
	Total	2500.933	14			
PCB 138 * Soil	Between Groups	382.767	3	127.589	.871	.485
	Within Groups	1612.167	11	146.561		
	Total	1994.933	14			
PCB 180 * Soil	Between Groups	140.767	3	46.922	.912	.467
	Within Groups	566.167	11	51.470		
	Total	706.933	14			

11.3 Affect of extraction conditions on relative recoveries.

During method development, we studied various factors that are known to affect sample recoveries. For example, $KMnO_4$ in acid conditions has been proven to be an effective clean-up strategy for PCBs headspace SPME with the advantage of removing most of the co-extracted organic species and elemental sulfur as well[3b, 45].

The following study was performed on Thermo PolarisQ GC-MS system. To study the matrix effect and absolute recovery of the method, empty glass vials were first spiked with liquid samples and dried before performing headspace SPME analysis. Secondly, this procedure was repeated, but with the addition of soil to the vials. Thirdly, the GC-MS instrument was calibrated using known quantities of liquid standards. The effect of matrix (soil) and modifiers such as $KMnO_4$ and H^+ on extraction efficiencies can be determined from the comparison of headspace standards under the different conditions.

Recoveries are largely affected by extraction time, fiber type, analyte volatility, solubility, and surface adsorption to particulates. Figure 9 and table 8 summarize the results of extraction time and the addition of wet chemicals on recoveries of selected PCBs. These results indicate that 30-minute extractions with acidified $KMnO_4$ provide significantly better extraction recoveries for soil than the other conditions studied. Agitation may have a weak benefit. These experiments were performed on the bench-top Thermo PolarisQ GC-MS.

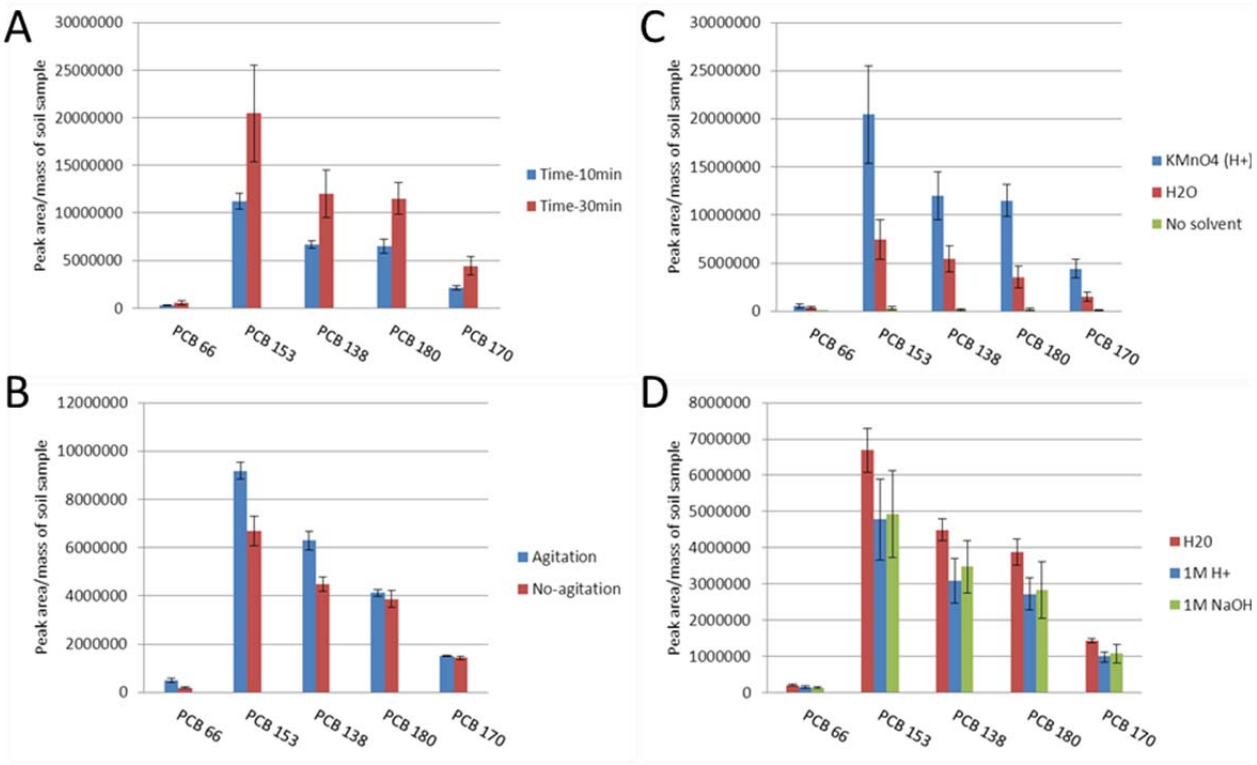

Figure 9. Effects of (A) SPME sorption time, (B) agitation, (C) addition of $KMnO_4$ and H_2O and (D) addition of acid and base on extraction efficiency of PCB 66, PCB 153, PCB 138, PCB 180 and PCB 170. Error bars show ±1 s.d. Significance tests are shown in **Table 5**.

Table 5. Paired t test results (the two tailed p-values) for the comparison of peak areas for five different PCB peaks under different conditions during headspace SPME extraction.

Condition of soil during headspace SPME sampling					
10 min vs 30 min	Agitation vs No agitation	$KMnO_4$ vs H_2O	H_2O vs Soil	H_2O vs H^+	H_2O vs OH^-
0.0433*	0.1128	0.0492*	0.0463*	0.0393*	0.0449*

*$p \leq 0.05$, difference exists

11.4 Absolute extraction recoveries

The absolute recovery of SPME extraction can be calculated by comparing the liquid injection results with SPME injection results. For Group 1, 50 µl 100 ppm standard solution of Aroclor 1260 was spiked to a 10 ml vial individually. Then all the standard samples were dried in the hood at room temperature. After sealing with caps, the samples were extracted

by SPME for 30 minutes at 100 °C and then ran in the instrument. For Group 2, the simulated soil sample (10 ppm, 0.5 g) was measured. 2.5 ml 0.2 M $KMnO_4$ and 0.25 ml 6 M H_2SO_4 were spiked into sample vial. The samples were sealed, vortexed, extracted by SPME for 30 minutes at 100 °C and then ran in the instrument. For Group 3, 1 µl 100 ppm Aroclor 1260 standard solution was injected to GC-MS. The split ratio was set to 50:1 for liquid injections, but unsplit for SPME. A correction for the split differences is taken into account. Each group was performed in triplicates. The results are plotted in Figure 10.

$$\text{Recovery (\%)} = \frac{ng\ detected\ (on\ column, via\ liquid\ cal.curve) - ng\ spiked}{ng\ spiked} \times 100\%$$

The ng detected is determined by comparing the peak area of each PCB from the SPME analysis to the corresponding calibration curve for each analyte from the liquid injections, taking into account the 50:1 split difference between the liquid and SPME injections.

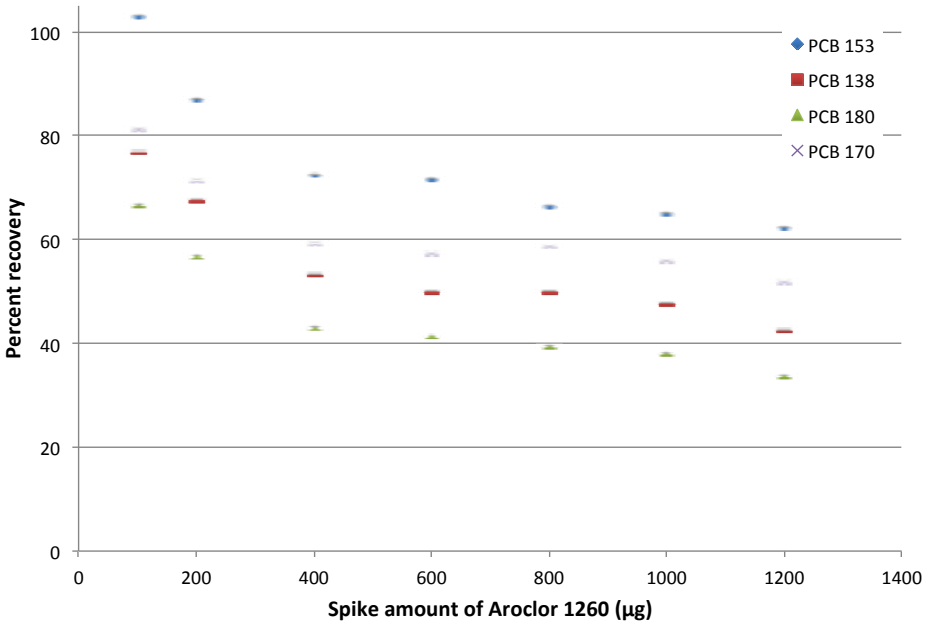

Figure 10. Effects of spike amount on the percent recoveries of selected PCBs in EPA 8082A mix in the absence of soil. The PCBs are extracted using headspace SPME and analyzed on the bench-top Polaris Q GC-MS (N=1).

Table 6. Summary of extraction efficiencies calculated using EPA 8082A mix.

PCB	No Soil (N=3)	With Soil (N=3)	P-value (two tailed T-test)
138	62%	16%	0.014*.
153	69%	26%	0.003*
180	63%	16%	0.014*
170	62%	16%	0.015*

*significantly different at 95% confidence interval

The absolute recovery results show that soil has the effect of decreasing the extraction efficiencies for headspace SPME from a typical efficiency of ~62% to ~16%, depending on the spike amount. When the PCB load is small, efficiencies are higher and more complete recovery is possible.

The superior precision of the bench-top instrument used in this recovery study enable significant differences to be determined. It is possible that if the first recovery study was repeated on the bench-top system, significant differences in the soil preparation method may be discernable.

11.5 Application to other Aroclors

The method established for Aroclor 1260 was tested on the other common Aroclors to provide evidence that the method can distinguish between them. Preliminary tests were performed on Aroclor spikes added to empty vials, in the absence of soil.

The chromatograms shown in Figure 11 indicate that some obvious differences between the TIC patterns in the resulting chromatograms. Extracted ion chromatograms could be used to help identify specific congeners (or co-eluting structural isomers), which could be used to manually differentiate between the different Aroclors. These chromatograms provide a proof of principal that Aroclor differentiation should be possible at the level of ~10 ppm (PCB in soil).

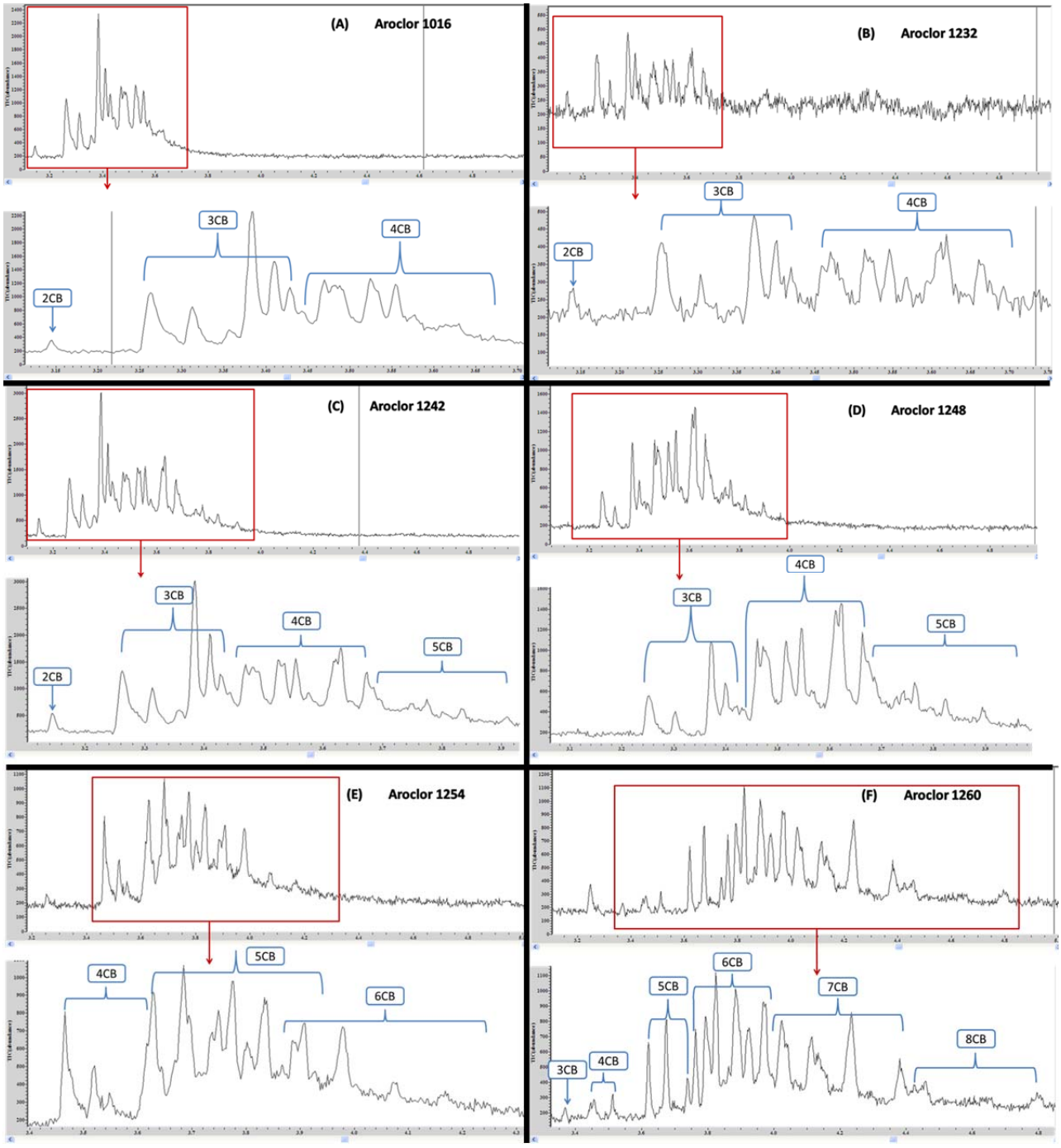

Figure 11. GC-TMS chromatograms (TIC) for headspace SPME analyses of 10 μg spikes of (A) Aroclor 1016, (B) Aroclor 1232, (C) Aroclor 1242, (D) Aroclor 1248, (E) Aroclor 1254 and (F) Aroclor 1260. The retention time windows of chromatograms for each Aroclor (upper chromatogram of each Aroclor) are fixed from about 3.1 min to 4.9 min. The lower chromatograms of each Aroclor show the same data in larger scale. (2CB: Dichlorobiphenyl; 3CB: Trichlorobiphenyl; 4CB: Tetrachlorobiphenyl; 5CB: Pentachlorobiphenyl; 6CB: Hexachlorobiphenyl; 7CB: Heptachlorobiphenyl; 8CB: Octachlorobiphenyl.).

12.0 DIOXINS AND FURANS

The headspace SPME method used for the various Aroclors was also applied to determine dioxins and furans. According to EPA method 8280B, dioxin and furan mix was purchased from AccuStandard Inc, which contained 5 dioxins and 5 furans. The dioxin mix standards were tested on the portable GC-TMS system. The GC program was optimized to 10 min. A spike consisting of 50 µl of 5 ppm dioxin and furan standard solution were added into 10 ml vial and dried in a fume hood. The samples were sealed and then extracted by SPME using 100 µm PDMS fiber for 30 minutes at 100 °C. The samples were analyzed using the Torion Guardion® portable GC-TMS system.

According to the results in Figure 12, 5 of the 10 compounds from the dioxin mix standard can be identified based on their retention times and mass spectra. The other 5 relatively heavy dioxin mix standards were not detectable. The main reason could be that the sensitivity of the instrument was much lower than bench-top instrument, especially for heavy dioxins. The other reason should be the extraction efficiency for heavy dioxins and furans was worse than lighter components.

The results of analyzing dioxins and furans by bench-top Thermo PolarisQ GC-MS system (Figure 13) demonstrated that the extraction efficiency of dioxins and furans from wet soil or dry soil with 2.5 ml 0.2 M $KMnO_4$ and 0.25 ml 6 M H_2SO_4 solution was extremely low. All the results above indicated that it was difficult to extract the dioxins and furans from soil using this method. By reviewing the literature, the extraction of dioxins and furans by SPME could be hardly found, which also indicates the difficulty of dioxin extraction from soil by this method.

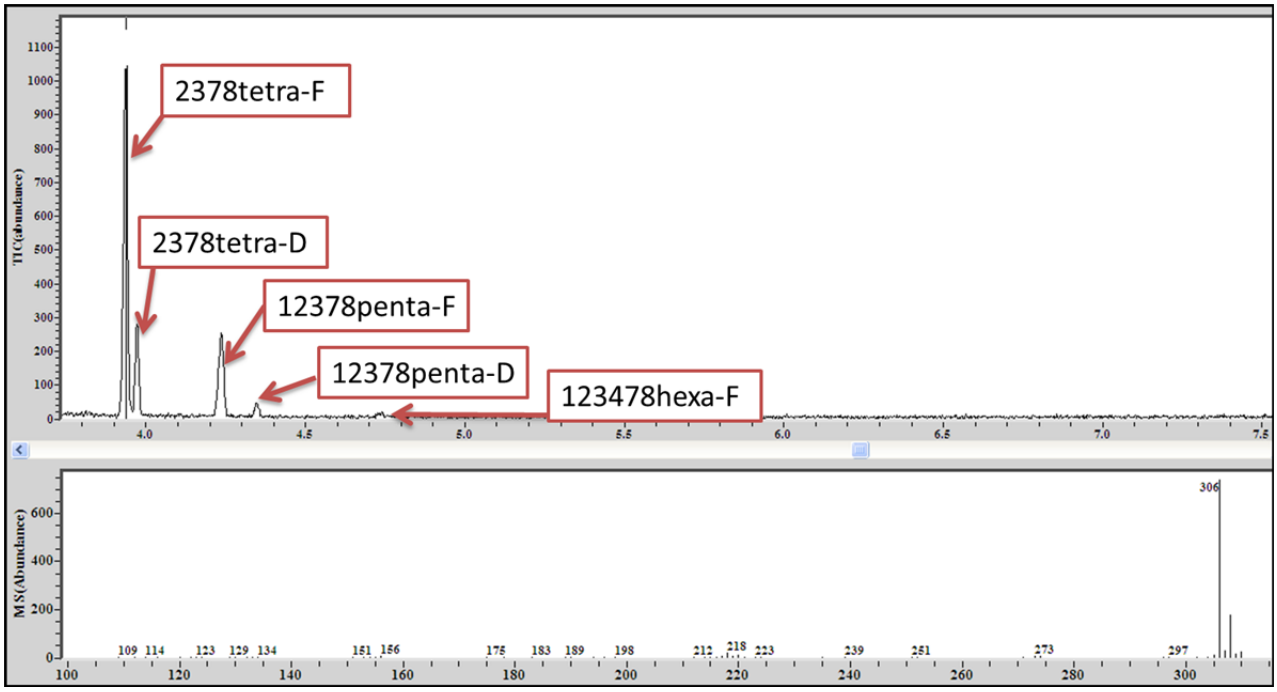

Figure 12. Dioxin mix standards tested on portable Torion Guardion® 8 GC-TMS system using headspace SPME extraction. Spike consisted of 50 µL of a 5 ppm stock solution of EPA 8280B mix in the absence of soil matrix.

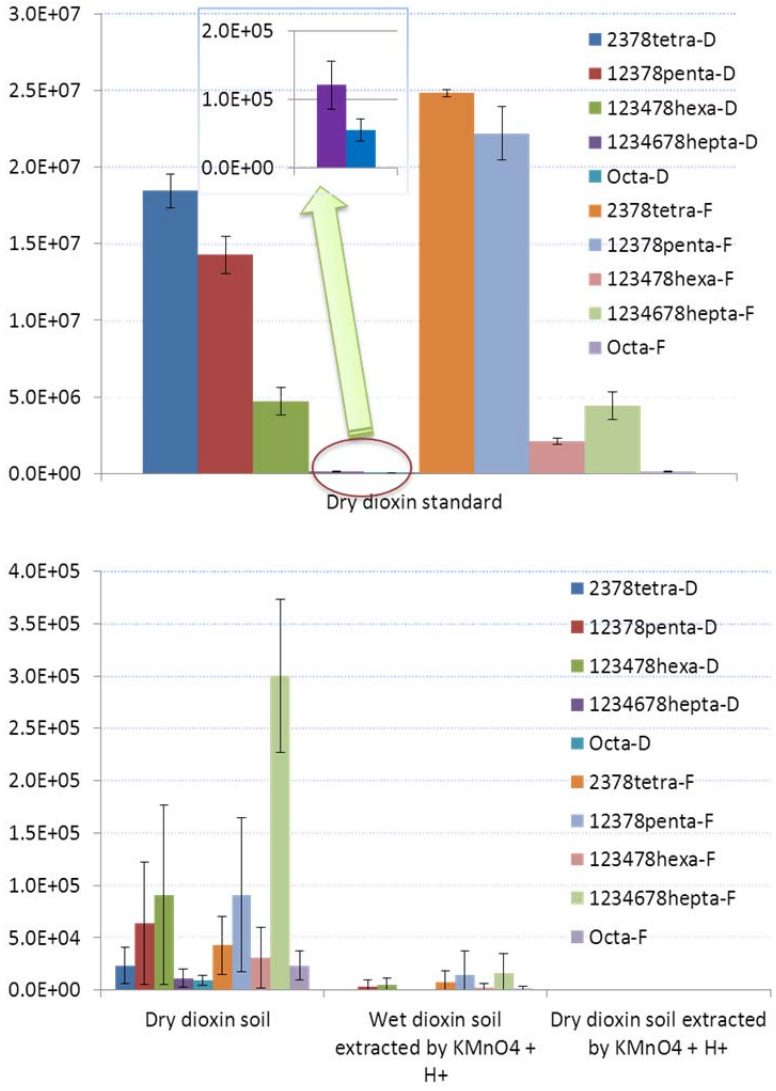

Figure 13. Dioxin mix standards tested on bench-top Thermo Polaris Q GC-MS system using headspace SPME extraction. Spike consisted of 50 μL of a 5 ppm stock solution of EPA 8280B mix with different matrices. The dry dioxin standard (top figure) was measured in the absence of any chemical modifiers or matrix. The dry dioxin-spiked soil (bottom figure), was analyzed with and without treatment with acidified $KMnO_4$. Wet dioxin-spiked soil (bottom figure) was also extracted following treatment with $KMnO_4$ + H^+.

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