Application of Automated Solid Phase Extraction for Determination of Polychlorinated Biphenyls (PCB) in Water

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Abstract

The determination of PCB in aqueous samples is an analysis carried out by many environmental testing laboratories. Traditional methodologies typically involve manual separatory funnel or continuous liquid-liquid extraction (CLLE) of the water samples with dichloromethane. Subsequently, the extract is dried using specially prepared anhydrous sodium sulfate, concentrated through an evaporation step, solvent exchanged to hexane, and analyzed using conventional split/splitless GC-ECD.

These methods are labor intensive, use large amounts of solvents, and require contaminate free glassware. Demands have been placed upon environmental testing laboratories to increase sample throughput, shorten sample turnaround times, achieve reproducible results, and provide lower detection limits.

NEA has met this challenge by optimizing a Solid Phase Extraction (SPE) method based on the Horizon Technology SPE-DEX 4790 instrumentation that is rugged, fast, cost effective, and achieves low MDLs and reproducible results. Horizon Technology SPE-DEX 4790 units are programmable multipurpose automated SPE systems, capable of processing aqueous samples directly from their original containers.

Once initiated, each SPE-DEX 4790 unit sequentially delivers all the necessary solvents to precondition the sorbent material within the SPE disk, passes the water sample through the disk and, after a preset air-dry time, extracts the sorbed analytes from the disk into a collection vessel using the required amounts of solvents. NEA routinely extracts 1-Liter, 2-Liter, 4-Liter and 8-Liter water samples using this technology.

NEA uses a modified congener-specific analysis, which employs a GC/ECD equipped with a DB-1 capillary column. This method utilizes a mixed Aroclor standard (Aroclor 1232/1248/1262 in the ratio of 25:18:18) for calibration based on the Green Bay Mass Balance method. A total of 112 chromatographic peaks are detected, containing 209 PCB congeners in various ratios. This allows an almost complete profile of environmentally occurring PCBs. This system allows for detection limits of 9.34ng/L for 1L samples and 1.06ng/L for 8L samples.

Introduction

The analysis of water for Polychlorinated Biphenyls PCBs has proved to be the most challenging matrix to implement the needs and wants of the end data users. Traditional methodologies typically involve manual separatory funnel or continuous liquid-liquid extraction (CLLE) of water samples with dichloromethane. The extract is concentrated through an evaporation step; solvent exchanged to hexane, and analyzed using split/splitless GC-ECD.

Theses methods were original developed for an Aroclor analysis and worked very well with highly contaminated samples. However, with the necessity of trace analysis for PCBs in water these methods are labor intensive, use large amounts of solvent, and require contaminant free glassware. Laboratories are limited in the number of samples they can process in a day and the reproducible results, and lower detection limits.
The purpose of this investigation/method development was to develop a new procedure for the determination of PCBs congeners in aqueous samples down to the low ng/L PPT range, with a minimum of organic solvent consumption.

We have developed a fast and rigorous sample extraction and cleanup techniques that is selective for the PCB congeners but can still be used for Aroclor PCBs, by optimizing a Solid Phase Extraction (SPE) method based on the Horizon Technology SPE-DEX 4790 instrumentation. The sample preparation is an essential part of this method development in conjunction with the instrumentation. The development of automated extraction and cleanup processes has resulted in less solvent use, less glassware and less extraction time.

**Methods and Materials**

For the extraction of (PCBs) from a water matrix, the procedure was developed based on EPA approved solid phase extraction (SPE) method, SW846 3535, which utilizes one liter of sample and less than 50 mL of solvents, methanol and methylene chloride.

NEA has tandem series of eight Horizon Technology SPE-DEX® 4790 automated extraction system. (see picture 1). These units allow the extraction of 1-liter, 2-liter, 4-liter and 8-liter water samples that has the capacity to process eight samples simultaneously or in any combination.

The water samples are extracted using styrene divinylbenzene extraction disks. The automated extraction system automatically pre-clean and activate the SPE disk, extract the water sample, and elute the PCBs from the disk into a collection vessel for further processing. The extracts undergo solvent exchange and clean-up procedures prior to analysis. NEA has done exhaustive PCB Congener MDL studies on these units.

**Apparatus and Reagents**

**Equipment:** Horizon SPE-DEX® 4790 automated extraction system and controller

**SPE Filters:** Bakerbond Speedisk DVB – Styrene divinylbenzene 50mm disk for sample extraction

**Reagents:** Hexane and Acetone Pesticide residue grade were obtained from Burdick & Jackson (Muskegon, Michigan). Methanol OmniSolv Pesticide residue grade was obtained from EM Science. Reagent Water – 18-megaohm water obtained from the laboratory’s water purification system. Sulfuric Acid, concentrated – Sulfuric acid is cleaned by washing with hexane prior to use. 1:1 Sulfuric acid – Prepared from solvent washed concentrated sulfuric acid.

**PCB Aroclor/Congeners**

**Aroclor 1242 Stock Standard at 990ug/mL in Hexane:**
The Aroclor 1242 stock standard is prepared from a neat Aroclor formulation (obtained from Monsanto directly) by weighing approximately 0.0990g and dissolving and diluting to volume in a 100mL volumetric flask with hexane.

**Mixed Aroclor Stock Standard at 62.7ug/mL:** A primary standard is prepared at 62.7ug/mL that is used for preparing secondary stock standards and calibration standards. This stock standard is prepared by combining Aroclor 1232, Aroclor 1248, and Aroclor 1262 in a 25:18:18 ratio with a final mixture concentration of 25.7ug/mL, 18.6ug/mL, and 18.4ug/mL respectively (total=62.7ug/mL). These ratios are strictly maintained so that the percent composition data remains applicable, since it was developed for use under these fixed mixture parameters.

The final concentration of the mixed standard may vary to accommodate instrument sensitivity or more closely represent sample concentrations, but the same ratio values are maintained.
Surrogate Stock Standard (2,2’,3,3’,4,4’,5,6,6’-Nonachlorobiphenyl) at 100ug/mL in Hexane: The surrogate stock standard is prepared from a solid standard obtained from AccuStandard, Inc.

Internal Standard Solution at 202ug/mL: The internal standard used for capillary gas chromatography of PCBs will be octachloronaphthalene (OCN). This is obtained as a solid from Ultra Scientific.

Solid-Phase Extraction
Solid-phase extraction was done with Horizon Technology SPE-DEX® 4790 automated extraction system. The extractor unit can accept 1-liter to 4 liter bottle (see picture 2 show a unit with a 1 & 4 Liter bottle setup). The SPE-DEX 4790 Extractor will automatically pre-wet the SPE disk, extract the sample, air dry the disk post extraction, and extract the disk to recover the analytes of interest.

The initialization and purge cycle of extractor system cleans and per condition the SPE Disk. During the time the SPE units were being prepared for extraction One Liter bottles were filled with Reagent Water – 18-megaohm water from the laboratory’s water purification system. The water was allowed to equilibrate for 30 minutes. The controller for the SPE-DEX 4790 Extractor starts the purge cycle that clean the extractor unit by dispensing the pre-wet solvents and directing them to the solvent recovery bottle.

The unit is set up with an empty clean 1-liter bottle, a pre-rinsed disk holder base onto the disk holder assembly and a collection vessel (40mL VOA vial and adapter) onto the bottom tapered joint of the disk holder assembly. The purge cycle will clean the extractor unit by dispensing the pre-wet solvents and directing them to the solvent recovery bottle.

Next the rinse solvents will be sprayed into the empty sample bottle and directed to the collection vessel. This cycle has five pre-wet steps which uses Hexane, Acetone and water respectfully and take about 6 minutes.

For the extraction of water samples the water must have a pH of 2. The acidify water improves the extraction of the PCBs. This done by adding 1.0mL of 1:1 sulfuric acid to every sample and all QC samples associated with the batch. Invert the sample container several times to mix, pH of the sample is less than 2. If not, then add 0.5mL more of 1:1 sulfuric acid until a pH of 2 is reached.

A new 50mm Bakerbond Speedisk DVB is installed onto the disk holder platform with a luer adapter. The water sample bottle is attached to the extractor unit with a 33 X 400 adapter bottle cap. The water is gravity fed into the SPE Disk by the Water-Inlet Delivery Valve (see picture 3).

The sample is allowed to pass onto the sorbent bed of the disk where the PCBs are retained on the bed. The water is then evacuated to the waste water reservoir. The time required is dependent on particulate loading and the flow through SPE disk. In general a river water sample takes 35 minutes while a Reagent Water – 18-megaohm water takes 20 minutes.

The down tube see (picture 4) carries the water sample to the SPE disk. Once the rising water prevents air from entering the bottle the water flow is temporarily stopped. More water enters the disk as the water is evacuated through the disk into the waste water bottle. The liquid level sensors (picture 4) determine the presence or absence of the water sample. When the entire sample is processed the bottom sensor is no longer cooled by being submerged and heats up, signaling the unit to proceed to the solvent extraction step.

Once all the water has passed through, the SPE disk is air dried. Solvents used for extraction of SPE Disk are done with Acetone and Hexane. The Acetone is sprayed upward into the sample bottle and the solvent drains down onto SPE disk. The disk is soaked for 1.5 minutes. The solvent is pulled by vacuum into a 40ml VOA vial. This process is repeated 3 more times with hexane.
The following table outlines the 8082.3 extraction method that the SPE-DEX 4790 Extractor unit uses to process and extract a water sample:

**Extraction Method 8082.3**

<table>
<thead>
<tr>
<th>Step Number</th>
<th>Procedure</th>
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| Pre-wet Step 1 | Solvent: Hexane  
Soak Time: 1:00 minute  
Air Dry Time: 0:30 minutes |
| Pre-wet Step 2 | Solvent: Acetone  
Soak Time: 1:00 minute  
Air Dry Time: 0:30 minutes |
| Pre-wet Step 3 | Solvent: Methanol  
Soak Time: 1:30 minutes  
Air Dry Time: 0:00 minutes |
| Pre-wet Step 4 | Solvent: Reagent Water  
Soak Time: 1:00 minute  
Air Dry Time: 0:00 minutes |
| Pre-wet Step 5 | Solvent: Reagent Water  
Soak Time: 1:00 minute  
Air Dry Time: 0:00 minutes |
| Sample extraction Step 6 | Time depends on particulates and sample flow through solid-phase filter |
| Air Dry Disk Step 7 | Air Dry Time: 5:00 minutes |
| Rinse Step 8 | Solvent: Acetone  
Soak Time: 1:30 minute  
Air Dry Time: 1:00 minute |
| Rinse Step 9 | Solvent: Hexane  
Soak Time: 1:30 minute  
Air Dry Time: 1:00 minute |
| Rinse Step 10 | Solvent: Hexane  
Soak Time: 1:30 minute  
Air Dry Time: 1:00 minute |
| Rinse Step 11 | Solvent: Hexane  
Soak Time: 1:30 minute  
Air Dry Time: 1:00 minute |

The amount of solvent used for the extraction 10mls per rinse step and takes approximately 20 minutes to run the whole extraction phase of the process. The sample extract will have two phases, the top layer will be composed of the hexane used to elute components from the solid-phase disk and the bottom layer will be composed of residual water and acetone from the extraction process. The sample top layer of solvent is transfer to a 60mL VOA vial.

The sample residual water/acetone is backwashed three successive times with hexane (approximately 5mL) and added to the extract. The sample is then concentrated to approximately 5.0mL. The samples is further processed with clean up of Florisil, sulfuric acid and mercuric precipiation. The sample is set to a final extract volume of 5mLs in hexane.

The first part of the extraction procedure of the sample through SPE extractor and trapping of the PCBs on SPE-disks, were thoroughly investigated. The removal of water was the most important step of the extraction process, since remaining water in the disk pores could inhibit solvent access to analytes at these locations. To succeed in this process, at low PCB concentrations, the cleaning of filters and optimization of the drying step were essential.

**GC Analysis**

NEA uses GC/ECD methodology for the analysis of PCB Congeners on a routine bases. This method is based on the Green Bay Mass Balance Study analytical technique. The method will effectively separate 116 or more peaks representing 209 PCB congeners a mixed Aroclor standard (Aroclor 1232/1248/1262 in the ratio of 25:18:18) for calibration. A key component of this method is the importance placed on the chromatographic separation that must be achieved for this congener specific technique.

This allows an almost complete profile of environmentally occurring PCBs DB-1 (J&W Company), bonded polydimethylsilicone, 30-meter fused silica capillary column with an internal diameter of 0.25mm and phase coating thickness of 0.25 microns. In environmental samples, which are known, to contain Aroclor based PCB contamination non-Aroclor congeners, which co-elute with Aroclor congeners, are assumed not to be present. This methodology achieves low MDLs (1 PPT (ng/L) for 8-liter samples and 9 PPT (ng/L) for 1-liter samples).
Method Summaries

SPE is a comparable method to more traditional methodologies of Separatory Funnel and continuous liquid-liquid extraction (CLLE). The uniqueness of SPE extraction is that it is rugged, fast and cost effective. SPE take 3.5 hours on average and 1 Technician, Separatory Funnel takes on average 10 hours and 2 Technicians, and CLLE takes on average 7 hours and 1 Technician for a sample set of 18 plus QC.

Utilization and cleaning of large 2 L separatory funnels and other glassware is completely eliminated by SPE. Samples can be processed in 35 minutes or less saving considerable labor costs for extraction. SPE workstations with 8 units are available for labs anticipating higher sample throughput.

The SPE procedure eliminates 90 percent solvents when compared with the conventional methods, exhibiting a significant reduction in purchase and disposal costs of chlorinated solvents such as methylene chloride. It also greatly increases safety in the laboratory by reducing potential exposure of workers to the solvents.