

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 requires 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. Northeast Analytical (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 were 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

Polychlorinated Biphenyls (PCB) are a worldwide contamination problem. Because PCBs are long lived in the environment and bioaccumulate through out the food chain a great deal of research and regulations has been implemented.

PCBs were first manufactured in the USA by Swan Corporation. By 1930's Monsanto had acquired Swan and was producing PCB mixtures under the trademark Aroclor (1). Several major US water bodies such as the Hudson River, St. Lawrence River, Fox River and the Great Lakes have been contaminated with PCB. Aroclor 1242, 1248 1254 and 1260 were the major sources of PCB contamination from industries discharging into these water bodies for decades.

The Aroclors that were discharged have undergone aerobic and anaerobic degradation, weathering, volatilization and sedimentation. The Aroclors no longer resemble the original mixture and pattern but PCB congeners that made the Aroclors are still present but in different amounts and altered patterns. With the improvement of laboratory techniques over the past 25 years investigators are looking closer at individual congeners instead of the Aroclor mixtures. With investigations of individual PCB congeners a shift in analysis has occurred from total Aroclor analysis to Congener Specific analysis with "Total PCB". This development has lead to a greater need for versatility in PCB analysis.

With tighter regulation and lower level detection limits being required by regulating authorities' analytical laboratories have to find improved methods of extraction and analysis. The challenge for any lab is meeting the client's/regulatory needs and wants of increase sample throughput, shorten sample turnaround times, achieve reproducible results, and to provide lower detection limits.

The analysis of water for 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. These 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 an eight Horizon Technology SPE-DEX® 4790 automated extraction system that has the capacity to process eight samples simultaneously. These units allow the extraction of 1-liter, 2-liter, 4-liter and 8-liter water 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, part number RCN-012.

Solid-Phase Extraction

Solid-phase extraction was done with Horizon Technology SPE-DEX® 4790 automated extraction system (Image 1.). The extractor unit can accept 1-liter to 4 liter bottle 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.



Image 1. 8-Unit Horizon Technology SPE-DEX® 4790 Systems

A Brief Overview of the Extractors

The initialization and purge cycle of extractor system cleans and pre-conditions the SPE Disk. During the time the SPE units were being prepared for extraction One Liter bottles were filled with Reagent Water – 18-megohm 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.

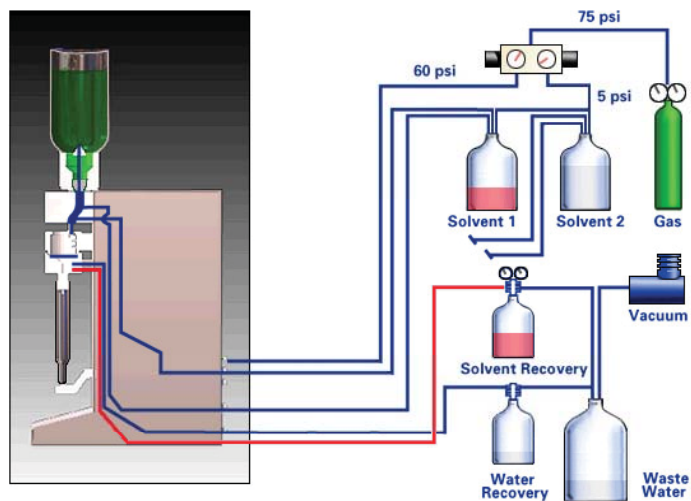


Figure 1: Initialization and Purge Cycle of Extractor System

For the extraction of water samples the water must have a pH of 2. The acidified water improves the extraction of the PCBs. This is 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. The 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. 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-megohm water takes 20 minutes.

The down tube 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 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. Solvent extraction of SPE Disk is 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, then the solvent is pulled by vacuum into a 40ml VOA vial. This process is repeated 3 more times with hexane (Figure 2).

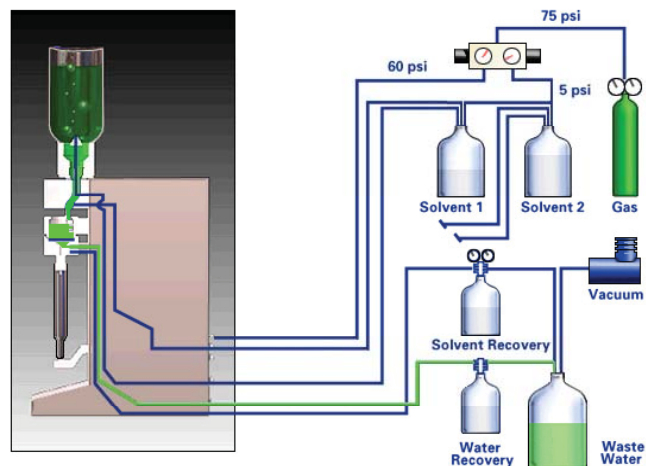


Figure 2: Sample Introduction for Extraction

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

Step Number	Procedure
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 is 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 (composed of the hexane used to elute components from the solid-phase disk) and the bottom layer

(composed of residual water and acetone from the extraction process). The sample top layer of solvent is transferred 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 in a TurboVap LV, to approximately 5.0mL. The samples are further processed with a clean-up of Florisil, sulfuric acid and mercuric precipitation. The sample is set to a final extract volume of 5mLs in hexane.

Experimental

For the development of this method several method detection limit (MDL) studies were run on Reagent Water – 18-megohm water and on river water. Seven laboratory organic free water samples were prepared with the mixed Aroclor calibration standard at a low level and taken through all extraction and analytical procedures. Method detection limit data was determined for each chromatographic peak (comprising one or more PCB congeners) based on the following equation:

$$MDL = S * t(n-1, 1-\alpha=0.99)$$

Where:

S = Standard deviation of the replicate analyses

n = Number of replicates

t(n-1, 1-alpha=0.99) = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = t(7,0.99) = 2.998

Analysis

NEA uses two GC/ECD methods for the analysis of PCB Congeners on a routine bases. These methods are both congener-specific determinations, employing a high-resolution fused-silica capillary chromatographic column. Both analytical methods have been used with samples extracted with SPE-DEX 4790 unit and the extraction method.

The first method is based on the Green Bay Mass Balance Study analytical technique. This method will effectively separate 116 or more peaks representing 209 PCB congeners of 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 from a 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 and non-Aroclor congeners, which co-elute with Aroclor congeners, are assumed not to be present.

The second method is a modified SW 846-8082 Comprehensive Quantitative Congener Specific (CQCS) method for PCB analysis that determines all 209 PCB congeners. The 209 PCB congeners are measured from 146 chromatographic peaks utilizing a mathematical deconvolution for PCB congeners that co-elute during GC analysis. PCB congeners, which exist at, trace levels (<0.05 weight percentage) are undetected in Aroclor formulations (approximately 62 congeners) can be reported by this method. The instrument calibration is achieved by using the 9 Calibration mixtures containing all 209 PCB congeners from Accustandard. This method is designed for the quantitation of total PCBs in samples resulting from both Aroclor type distributions and weathered, degraded, or non-Aroclor like distributions. Visual identification of Aroclor patterns (if present) may be possible in some cases by chromatographic comparison of samples with reference standards. A sum total of PCB present in the sample is provided by this method.

Results

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 takes 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 of the 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.

The Green Bay Methodology achieves low MDLs (1 PPT (ng/L) for 8-liter samples and 9 PPT (ng/L) for 1-liter samples)

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