

DETERMINING POLYCHLORINATED BIPHENYL (PCB) CONGENERS IN WATER UTILIZING AUTOMATED SPE

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Introduction:

The purpose of this investigation/method development was to establish a new extraction method using hexane as the extraction solvent for the determination of 209 PCB congeners in 116 chromatographic peaks in various ratios in aqueous samples which would allow for a detection range into the ng/L (PPT) range for 1L and 8L samples while processing the samples through the disk at over 100 mL/min. This was accomplished by optimizing a Solid Phase Extraction (SPE) method based on the Horizon Technology SPE-DEX® 4790 Automated Extractor System using a divinylbenzene (DVB) extraction disk and detection through a GC/ECD. The sample preparation step is an essential element of this method development, and as such, the advancement of an automated disk extraction has resulted in less solvent use, elimination of the solvent exchange step, reduced glassware use, faster extraction time with highly particulate samples, and more consistent and reproducible results.

Materials and Methods:

Instrumentation and materials used in this study consisted of Horizon Technology's SPE-DEX® 4790 Automated Extractors with an Envision Controller and divinylbenzene (DVB) SPE Disks for the sample preparation. The analysis was conducted with an Agilent 6890GC with Micro ECD with a J&W Column: Primary- DB-1, 30 m x 0.25 mm ID x 0.25 µm film. Reagents: Hexane and acetone pesticide residue grade were obtained from Burdick and Jackson. Methanol OmniSolv pesticide residue grade was obtained from EM science. Reagent water was 18-megohm was obtained from the laboratory's water purification system. Concentrated sulfuric acid was cleaned by washing it with hexane prior to use. 1:1 Sulfuric acid was prepared from the solvent washed concentrated sulfuric acid.

The Aroclors 1232, 1248 and 1262 are mixed in the ratio of 25:18:18 for calibration curve and continuing check standards. 2, 2',3, 3',4, 4',5, 6, 6' nanachlorobiphenyl was used as the sample surrogate and octachloronaphthalene (OCN) was used as the internal standard. Each congener in the mix is measured and all 209 congener are in 116 chromatographic peaks. Aroclor 1242 is used as the LCS spike for waters using SPE and measures all the congeners present and sum them for total PCB and relate it back to the concentration of the Aroclors.

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.

Automated SPE-DEX 4790 extractor units allow the extraction of 1-liter, 2-liter, 4-liter and 8-liter water samples for obtaining lower detection limits. The water samples are extracted using divinylbenzene (DVB) extraction disks. The automated extraction system automatically pre-clean and activate the SPE disk, extracts the water sample, and elute the PCBs from the disk into a collection vessel. The sample is further processed with clean up of florisil, sulfuric acid and mercuric precipitation. After cleanup the sample is set to a final extract volume of 5mLs in hexane and ready to be analyzed by GC/ECD.

The GC/ECD methodology for the analysis of PCB Congeners 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). Green Bay PCB Standard at various levels: 37.6ng/L, 157ng/L, 627ng/L were used in this study.

To show the efficiency of the automated SPE extraction the spike was added to the DryVap concentrator to find out what typical recoveries would be in an ideal situation. Five samples containing 200 mL of DCM, 1 mL of water and PCB congeners spike mix were automatically dried and concentrated with the DryVap® system. The water was added to simulate residual water levels found in environmental extracts. The “wet” sample was poured into the reservoir and the system was started with a heating and reduced to a final volume of 1.0 mL. After drying and reducing the sample volume to 1 mL, 20 uL of nonane was added and the sample was processed further to a final volume of 20 uL. Carbons 13 labeled congeners were added as internal standards and the concentrate was analyzed by HRGC-HRMS.

Results and Discussion:

The results are excellent for all of the selected persistent organic polluting PCB congeners concentrated down to 1.0 mL on the DryVap®. If there was to be any loss of PCBs it would be during the extraction. The average recovery levels range from 95% for hexachlorobiphenyl (#169) to 112% for dichlorobiphenyl (#15.) from the 209 congeners. The average standard deviation for the entire data set is 4.3.

The results of this testing illustrates the method detection limits (MDL) for two initial sample volumes. The results show that this methodology is able to achieve low MDLs of 0.97 ppt for 8-liter samples and 9.34 ppt for 1-liter samples for total PCB. A total of 116 chromatographic peaks were detected, containing 209 PCB congeners in various ratios. This allows an almost complete profile of environmentally occurring PCBs and shows that the SPE-DEX automated extractor can not only process samples at over 100 mL/min but can retain PCB's congeners at a low ppt level with a fast sample flow rate.

This method shows that with tighter regulation and lower detection limits being required by regulating authority's analytical laboratories have to find improved methods of extraction and analysis. The challenge for any laboratory is meeting regulatory needs and wants of increased sample throughput, shorten turn around times and achieve reproducible results while providing lower detection limits. With this method based from Automated SPE by GC/ECD detection those requirements can be met.

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