Accelerated Solvent Extraction for Monitoring Persistent Organic Pollutants in Ambient Air

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Executive Summary

Persistent organic pollutants (POPs) in ambient air must be monitored for the best interests of public health. Polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) are two classes of organic pollutants that have demonstrated toxic effects in humans and are subject to monitoring by regulatory agencies such as the U.S. Environmental Protection Agency (EPA). The monitoring process consists of the use of air sampling cartridges to trap the pollutants, elution from the filters using organic solvents, and analysis by gas chromatography. Use of the accelerated solvent extraction technique has been demonstrated to significantly reduce the amount of time and solvent required to elute the pollutants from air filters and is considered a favorable alternative to the traditional Soxhlet procedure that is often used.

Keywords

Accelerated solvent extraction technique, ASE, Soxhlet, Polyurethane Filters, Polychlorinated Biphenyls, Polyaromatic Hydrocarbons, U.S. EPA Method TO-4, U.S. EPA Method 608, XAD Resins

Introduction

Air pollution refers to the mixture of solid particles, gases, and aerosols found in ambient air that are potentially hazardous to humans and wildlife. These compounds may be fine particulate matter, inorganic ions (e.g. nitrate, sulfate) or large organic pollutants (e.g. polyaromatic hydrocarbons). The level of toxic organic compounds is of particular concern in ambient air. Due to their long half lives and insolubility in water, these compounds have a high degree of stability and persistence in the environment. Many of these persistent organic pollutants have been shown to exhibit deleterious effects to humans and are categorized as carcinogens, mutagens, and/or teratogens. Due to the toxicity of these compounds, agencies such as the U.S. EPA have established monitoring guidelines to access levels in the environment. While environmental matrices such as soil, sediment, and tissue have received a lot of attention for monitoring, air is also a matrix that can be analyzed for the presence of organic pollutants.

Polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) are two classes of persistent organic pollutants that are monitored in ambient air. Each class of compounds present a myriad of health risks to humans and wildlife and are often sampled from the environment for monitoring. Traditional testing techniques for air samples rely on cartridges than capture the pollutants, elution procedures that remove the trapped pollutants and analysis by gas chromatography. The bottleneck in the process is the extraction of analytes from the cartridges. Traditionally the extraction has been performed using the Soxhlet technique, an effective but time consuming technique. More recently, the use of the accelerated solvent extraction technique was evaluated to streamline the elution step by reducing the amount of time and solvent required for the extraction. This newer technique has been shown to produce equivalent performance to Soxhlet while substantially reducing the amount of time and solvent consumption. This white paper compares the use of accelerated extraction technique for extraction of PCBs and PAHs from air sampling cartridges and compares the extraction efficiency against the Soxhlet technique.

Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a group of chemicals that contain 209 individual compounds known as congeners. PCBs were widely used as coolant and dielectric fluids for capacitors and transformers. These compounds have been demonstrated to cause cancer in laboratory animals and for this reason the U.S. EPA has classified PCBs as a Group B2 probable human carcinogen. Due to the toxicity of these compounds, the production of PCBs was banned by the United States Congress in 1979 and by the Stockholm Convention on Persistent Organic Pollutants in 2001.[1] Although PCBs are no longer produced, they are highly persistent in the environment and regulatory agencies such as the U.S. EPA have established methods for monitoring their presence in environmental matrices.

U.S. EPA Method TO-4 has been used for a number of years for the determination of PCB compounds in air. Sampling is performed by pumping a volume of air through a polyurethane foam (PUF) adsorbent cartridge in order to absorb any PCB congeners that may be present. Once trapped, these contaminants are eluted from the PUF cartridge using an organic solvent and analyzed by gas chromatography. The extraction from the PUF absorbent is typically performed using the Soxhlet technique according to the U.S. EPA Method 3540. This extraction method requires 12-14 hours of extraction time and 350 mL of solvent per sample. Once PCB congeners are eluted from the PUF cartridge, they are analyzed by GC-ECD by U.S. EPA Method 608.

While the Soxhlet extraction technique has been demonstrated to be effective in eluting PCB congeners from PUF cartridges, it is time consuming and costly for the environmental laboratory. Due to the size of the size of PUF cartridges (26–76 mm), the accelerated solvent extraction technique can be used to significantly reduce the amount of time spent on extraction. The accelerated solvent extraction technique has been compared to Soxhlet extraction followed by analysis with GC-ECD in Thermo Scientific Application Note 333: Accelerated Solvent Extraction (ASE) of Polychlorinated Biphenyls from Polyurethane foam Adsorbent Cartridges.[2] In this application, PUF cartridges were spiked with both a commercial mixture of PCB congeners (Aroclor 1248) and individual PCB congeners. In both instances, the accelerated solvent extraction technique demonstrated equivalent performance to the Soxhlet technique but required only 30 mL of solvent and 12 min per sample.

Tables 1 and 2 show the results of using accelerated solvent extraction technique followed by analysis with gas chromatography — electron capture detection for PUF cartridges spiked with Aroclor 1248 and individual PCB congeners. Table 1 displays the results of a laboratory capability study wherein PUF cartridges were spiked with 5.00 µg of Aroclor 1248. Four samples were spiked and then analyzed according to the conditions specified in U.S. EPA Method 608. The accelerated solvent extraction technique demonstrated lower recovery of Aroclor 1248 (90%) versus the Soxhlet technique (96%) but was well within the acceptance criteria for U.S. EPA Method 608 (38–158%). to be equivalent to Soxhlet and within the acceptance criteria of U.S. EPA Method 608.

Table 1. Comparison of spike recoveries between ASE and Soxhlet extraction of PCB congeners from PUF Cartridges.*

Sample #	Accelerated Solvent Extraction Technique Recovery (µg)	Soxhlet Recovery (µg)	U.S. EPA Method 608 Acceptance Criteria
1	4.63	4.87	
2	4.44	4.93	
3	4.72	5.16	
4	4.10	4.26	
Average(µg)	4.47	4.80	3.42–8.40 µg
Average Recovery	90%	96%	38–158%
Standard Deviation	0.274	0.384	<1.23

*Recoveries are based on spiked value of 5.00 µg Aroclor 1248

Table 2 shows the results of spiking PUF cartridges with individual PCB congeners. Eight congeners were spiked at levels between 5 – 10 µg and an average recovery of 99.5% with an average %RSD of 1.9 (n=5) was achieved.

Table 2: Recovery of PCB congeners from spiked PUF cartridges using Accelerated Solvent Extraction Technique.

Congener	BZ#*	Spike (µg)	% Recovery	%RSD (n=5)
2-chlorobiphenyl	1	5	100.4	2.3
2,3-dichlorobiphenyl	5	5	100.3	2.0
2,4,5-trichlorobiphenyl	29	5	102.2	1.8
2,2,4,6-tetrachlorobiphenyl	50	10	97.0	1.2
2,2,3,4,5-pentachlorobiphenyl	87	10	96.1	0.82
2,2,4,4,5,6-hexachlorobiphenyl	154	10	97.9	1.3
2,2,3,4,5,6,6-heptachlorobiphenyl	188	10	98.9	1.4
Decachlorobiphenyl	209	15	103.1	4.0

*BZ# = Ballschmitter number used to identify specific congeners.

Polyaromatic Hydrocarbons (PAHs)

Polyaromatic hydrocarbons (PAHs) are a potent atmospheric and widespread environmental pollutant. The presence of PAHs in ambient air results from the incomplete combustion of fossil fuels, wood, coal, diesel, tobacco, and incense. These differing types of combustion yield different distributions of PAHs in both relative amounts of individual PAHs and in which isomers are produced. Thus, coal burning produces a different mixture than motor-fuel combustion or tobacco smoke. The toxicity associated with PAHs are linked to specific isomers some of which have been classified as carcinogens, mutagens, and teratogens. The U.S. EPA has designated 16 PAH compounds as priority pollutants (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]flouranthene, benzo[a]pyrene, dibenz(ah)anthracene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene). This list of the 16 U.S. EPA priority PAHs is often targeted for measurement in environmental samples including ambient air.

PAHs are captured from air using XAD resins, a macroporous styrene divinyl benzene polymer that is loaded into a cartridge used for sampling. Once the PAH compounds are trapped on the resin, they are eluted with organic solvents and analyzed by gas chromatography — mass spectrometry (GC-MS). When these resins are received from the manufacturer, they are wet and contain background contaminants and thus require a cleaning step prior to use. The cleaning step requires large amounts of organic solvent that use three consecutive Soxhlet extractions using methanol, acetonitrile, and dichloromethane as extraction solvents. This procedure requires 15–24 h and 900–1500 mL of solvent per sample to complete. Following the cleaning procedure, the resins are packed into a XAD cartridge and used to collect PAH compounds from air. After PAH samples are collected, elution of PAH compounds takes 5–8 h and uses 300–500 mL of hexane/acetone (1:1) per sample. Collectively, the process takes 30 h and requires up to 2 L in organic solvent to complete.

Thermo Scientific Application Note 347: Use of Accelerated Solvent Extraction for Cleaning and Eluton of XAD Resin[3] compared the accelerated solvent extraction technique with Soxhlet extraction by measuring the time and solvent amount for the cleaning and elution steps of XAD resins. Additionally, cleaned XAD resins were spiked with 100 ppm of a PAH standard and the percent recoveries were determined following analysis by GC-MS. The results from the evaluation are shown in Tables 3 and 4. The use of the accelerated solvent extraction technique total solvent consumption went down to 550 mL and total extraction time down to three hours versus Soxhlet which required a total 20–32 h and 1200–2000 mL of solvent. The percent recovery of 15 spiked PAH compounds in cleaned XAD resins averaged 97.6% for five samples of each.

Table 3. Time and solvent use comparison (Accelerated Solvent Extraction Technique vs Soxhlet).

	Soxhlet Technique	Accelerated Solvent Extraction Technique
Solvent Consumption Cleaning	900–1500 mL	87.5 mL
Time Used for Cleaning	15–24 h	2.5 h
Solvent Consumption Elution	300–500 mL	50 mL
Time Used for Elution	5–8 h	18 min
Total Solvent Consumption	1200–2000 mL	550 mL
Total Time Used	20–32 h	3 h

Table 4. PAH recovery in XAD resins.

Compound	Recovery (% of Spike)
Acenaphthene	86.6
Acenapthalene	85.8
Anthracene	99.3
Benzo(a)anthracene	102.9
Benzo(b)fluoranthene	102.4
Benzo(g,h,i)perylene	101.1
Benzo(k)fluoranthene	103.7
Chrysene	103.4
Dibenz(a,h)anthracene	101.4
Fluoranthene	98.9
Fluorene	92.3
Indeno(1,2,3-cd)pyrene	100.7
Naphthalene	81.0
Phenanthrene	99.2
Pyrene	103.4

Conclusion

Extraction of persistent organic pollutants from air sampling cartridges is an essential part of current air monitoring regulations. However, currently used extraction methods are both time consuming and solvent intensive. The accelerated solvent extraction technique has proven to yield equivalent results to the traditional Soxhlet procedure while using less time and solvent. The accelerated solvent extraction technique takes advantage of enhanced solubilization kinetics that occurs at temperatures higher than what are commonly used to perform solvent extractions. As the efficiency of the extraction process is improved, less solvent and less time are required to complete the process. Since reducing solvent consumption and increasing sample throughput are important concerns to modern laboratories, the accelerated solvent extraction technique offers significant advantages for both the production and research laboratory that are performing extraction of air filters for pollution monitoring.

References

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WP71064_E 04/14S