Use of Accelerated Solvent Extraction for Cleaning and Elution of XAD Resin

Introduction

XAD resins are used as solid phase extraction materials for applications in water and air sampling. The resin, a macroporous styrene divinyl benzene polymer, is loaded into cartridges that are taken to the field for sampling. Once the resin has been used for sampling, the analytes are eluted with organic solvents and the eluates are concentrated and analyzed by GC/MS.

When resins are received from the manufacturer, they are wet and contain contaminants that make them unsuitable for immediate analytical use. The current methods for cleaning and eluting XAD resin require large amounts of solvent and time. Cleaning usually consists of three consecutive Soxhlet extractions using methanol, acetonitrile, and dichloromethane. This cleaning process takes 15–24 h and uses 900–1500 mL of solvent. Traditionally, after the resin has been cleaned and used for sampling, it is eluted with another Soxhlet extraction using hexane/acetone (1:1). This elution process takes 5–8 h and uses 300–500 mL of solvent. This results in a total cleaning and elution time of more than 30 h, and requires up to 2 L of solvent. Although the current cleaning and elution technique may yield acceptable results, it is obvious that it is not time- or cost-efficient.

Accelerated solvent extraction yields the same, if not better, results compared to Soxhlet methods, and achieves this faster while using considerably less solvent. Accelerated solvent extraction uses a combination of increased temperature and pressure to enhance the kinetics of the extraction process. Accelerated solvent extraction uses the same solvents as current extraction methods but with minimal exposure to the lab technician.

In this Application Note, an XAD-2 resin manufactured by Supelco is cleaned using accelerated solvent extraction. The clean resin is then spiked with organochlorine pesticides (OCP) and polyaromatic hydrocarbons (PAH) standards and eluted using accelerated solvent extraction. The results show that accelerated solvent extraction effectively and efficiently cleans and dries the resin without damaging the particles, and is able to elute OCP and PAH compounds from XAD resin with good results.

Equipment

- Thermo Scientific™ Dionex™ ASE™ 300 Accelerated Extractor System* with Solvent Controller (P/N 056764)
- 34 mL and 100 mL stainless steel extraction cells (P/Ns 056690 and 056691)
- Cellulose Filters (P/N 056780)
- Collection Bottles (P/N 056284)
- Analytical Balance (to read to nearest 0.0001 g or better)
- Solvent Evaporator

*Dionex ASE 150 and 350 systems can be used for equivalent results

Solvents

Hexane

Acetone

(All solvents are pesticide-grade or equivalent and available from Fisher Scientific.)

Extraction Conditions	
XAD-2 Cleaning	
Solvent:	Single Extraction with 100% Acetone Single Extraction with 75/25 Acetone/Hexane Two or three Extractions with 50/50 Acetone/Hexane
System Pressure:	1500 psi*
Temperature:	75 °C
Static Cycles:	5
Static Time:	5 min
Flush:	150%
Purge:	120 s
Extraction cell:	100 mL
Total Time:	2.0–2.5 h
Total Solvent:	500 mL

XAD-2 Cleaning	
Solvent:	Hexane/Acetone (1:1)
System Pressure:	1500 psi
Temperature:	75 °C
Static Cycles:	3
Static Time:	5 min
Flush:	150%
Purge:	120 s
Extraction Cell:	34 mL
Total Time:	18 min
Total Solvent:	50 mL
Total Solvent:	500 mL

*Pressure studies show that 1500 psi is the optimum extraction pressure for all accelerated solvent extraction applications.

XAD-2 Cleaning Procedure Using Accelerated Solvent Extraction

Place a cellulose filter into a 100 mL cell before filling with resin. Weigh 45–50 g of XAD resin into the 100 mL cell, and hand-tighten the end caps. Enter three different cleaning methods into the method editor screen: Method #1 using 100 % acetone; Method #2 using 75/25 acetone/hexane; and Method #3 using 50/50 acetone/hexane. (Note: Use of a solvent controller allows the solvents to be mixed automatically for each method. No pre-mixing is required.) All three methods use the extraction conditions listed above. The schedule should consist of five extractions of each cell as follows: Method #1; Method #2; and three extractions with Method #3. Because five extractions are required for the cleaning of the resin, two 100 mL extraction cells containing approximately 100 g total of XAD resin can be cleaned per automated run.

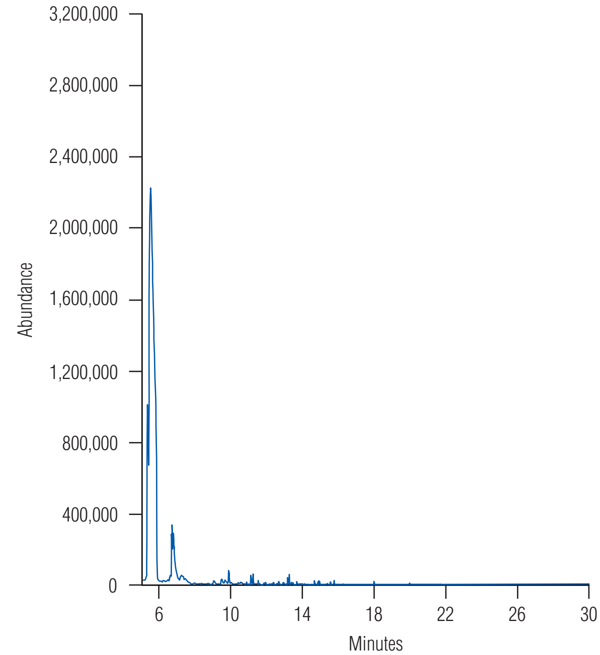

Figure 1. Dionex ASE system blank GC/MS run.

XAD-2 Cleaning Procedure Using Accelerated Solvent Extraction

Place a cellulose filter into a 34-mL cell. Weigh approximately 16 g of pre-cleaned XAD-2 resin, or the contents of the field-sampling device, into the cell. Spike the resin with desired internal compounds, or surrogate compounds. Place the end cap on the cell and load onto the Dionex ASE 300. Set up the elution method as described above and begin the extraction.

The extracts can then be concentrated using a solvent evaporator to the desired level or for solvent exchange. The extracts are then ready for GC analysis.

Results and Discussion

In this evaluation, there was concern that the elevated temperature used in accelerated solvent extraction may adversely affect the XAD resin particle. This process, known as cracking, disrupts the particle surface, and can be monitored via the release of naphthalene. The temperature of 75 °C was chosen for the cleaning and elution methods because prior analysis showed no or very low naphthalene levels present in the extracts.

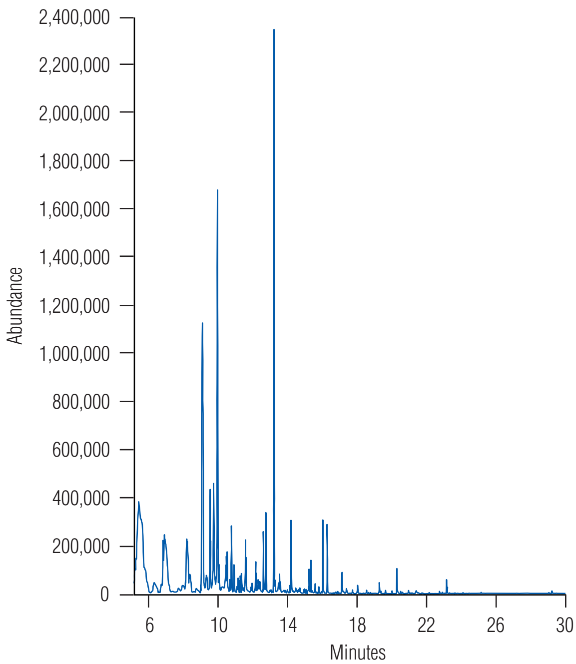

Figure 2. Raw XAD resin extraction.

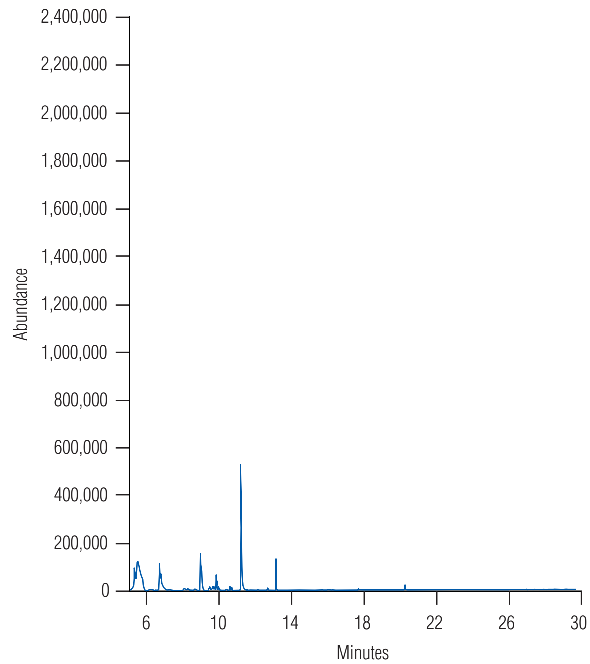

Figure 3. Clean XAD resin extraction.

When developing a method to clean and dry the XAD-2 resin, a clean resin was defined as a flat GC/MS and GC/ECD baseline with less than 20 pg material injected onto the column. This definition was developed using standard Soxlet extraction. An initial extraction with 100% acetone removed most or all of the water present on the resin. The next extraction used a 75/25 acetone/hexane mixture to begin to remove some polar and non-polar compounds. The final extraction used 50/50 acetone/hexane mixture and was repeated three times. Depending on the cleanliness level of the resin, three extractions may not be necessary. Figure 1 is a chromatogram of the Dionex ASE system blank GC/MS run. Figure 2 is a chromatogram of the accelerated solvent extraction of raw XAD-2 resin before cleaning. This was extracted with 100% acetone at 75 °C. Figure 3 is a chromatogram of the final extract of the accelerated solvent extraction cleaning procedure developed for the XAD-2 resin. The results show a significant decrease in resin contaminants and the resin was then considered clean.

Once a method to clean the resin had been established, a method for elution of the resin was developed. The strategy was to spike the clean resin directly with PAH and OCP standards. The PAH compounds were added at 100 ppm and the OCP compounds were at 10 ppb. The spiked resins were eluted with hexane:acetone 1:1 at 75 °C, and the PAH extracts were analyzed by GC/MS, while the OCP were analyzed by GC/ECD. Table 1 shows the percent recoveries of the OCP standard compounds, with an average compound recovery of 84.6%. Table 2 shows the percent recoveries of the PAH standard compounds with an average compound recovery of 97.6%.

Table 1. Accelerated solvent extraction of XAD resin: Recovery of OCP spike.

Compound	Recovery (% of Spike)
Aldrin	87.5
BHC	71.8
BHC	83.3
Lindane	74.7
4,4-DDD	93.0
4,4-DDE	85.4
4,4-DDT	86.7
Dieldrin	91.5
Endrin	84.1
Heptachlor	79.3
Heptachlor Epoxide	92.8

Table 2. Accelerated solvent extraction of XAD resin: Recovery of PAH spike.

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

Average PAH Recovery = 97.6%

Table 3. Time and solvent savings by using accelerated solvent extraction compound.

	Soxhlet	ASE
Solvent Consumption Cleaning	900–1500 mL	87.5
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

Conclusions

The Dionex ASE system was able to efficiently clean and elute XAD resin, with good recoveries of PAH and OCP spike solutions, requiring less than half the time and using significantly less solvent than the traditional methods. Table 3 compares time and solvent savings of this accelerated solvent extraction method to the traditional Soxhlet method. Other researchers have also had success eluting polychlorinated dibenzodioxins (PCDDs) and polychlorinated biphenyls (PCBs) from XAD resin using accelerated solvent extraction.[1]

Reference

1. Yang, J. et al. Bull. Korean Chem Soc. 1999, Vol. 20, no. 6, 689–695.

Suppliers

Fisher Scientific, 711 Forbes AVE., Pittsburg, PA 15219, USA, 412-562-8300

Acknowledgement

Thanks to Edward Sverko at the National Laboratory for Environmental Testing, Burlington, Ontario, Canada for his collaboration.

Australia +61 3 9757 4486
Austria +43 1 333 50 34 0
Belgium +32 53 73 42 41
Brazil +55 11 3731 5140
China +852 2428 3282
Denmark +45 70 23 62 60
France +33 1 60 92 48 00
Germany +49 6126 991 0
India +91 22 6742 9494
Italy +39 02 51 62 1267
Japan +81 6 6885 1213
Korea +82 2 3420 8600
Netherlands +31 76 579 55 55
Singapore +65 6289 1190
Sweden +46 8 473 3380
Switzerland +41 62 205 9966
Taiwan +886 2 8751 6655
UK/Ireland +44 1442 233555
USA and Canada +847 295 7500