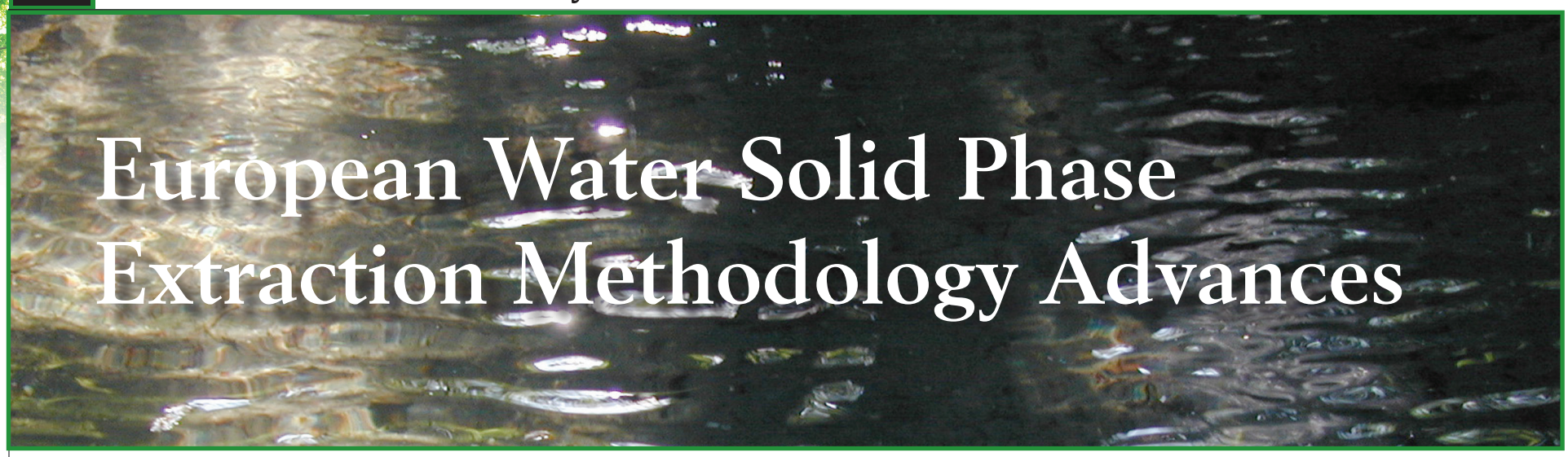

European Water Solid Phase Extraction Methodology Advances

Analysis is critical for environmental protection, and water is one of the most important media to monitor. Water provides approximately 60% of the environmental samples by media and is especially important because it provides a large source of exposure for human and animal life.(1) Water analysis for pollutants should be reliable and allow detection at low levels necessary for decision-making. Extraction of the analytes from the water sample prior to instrumental analysis is generally required to separate any interferences and concentrate analytes. Environmental analytical techniques generally used for semivolatile organic compounds are gas chromatography (GC) with a specific detector, such as an electrolytic conductivity detector (ECD) or more general mass spectrometer (MS) when a variety of compounds is to be determined. Extraction can be accomplished with a liquid-liquid extraction with a solvent such as dichloromethane (DCM) or by using solid phase extraction to adsorb the analytes from the water and then elute them into a suitable solvent.

"The European Union has taken the first steps to incorporate disk solid phase extraction as an option in their water sampling and analysis program. These examples show that there are other options to also consider as they move forward to expand disk use and address more complex samples and issues."

Solid phase extraction provides several advantages over liquid-liquid extraction including using less solvent and avoiding emulsion creation. In addition, it can more easily be automated, further improving reproducibility between technicians and reducing exposure to solvent. Solid phase sorbents are available in a variety of formats with cartridges being one of the more popular and very suitable for food and pharmaceutical analyses. Disks are more suitable for larger-volume samples and for samples that may have particulates, such as many samples encountered in environmental analysis.

The European Union is moving to adopt newer technology based on solid phase extraction (SPE) that will allow larger samples to be easily extracted, making flexibility in achieving lower detection limits possible.(2) Several methods that have been recently developed and their status are listed in Table 1. These use SPE disks to allow the rapid extraction of semivolatile analytes for subsequent instrumental analysis.

These methods are designated for whole water which generally contains a small amount of particulate matter. Solid phase extraction can also provide advantages for more heavily particulated samples, such as wastewater. Disk SPE can handle a larger percentage of solid material without clogging or taking an excessively long time to flow through the disk. Pre-filtering the sample is impractical as it would remove some analytes bound to the particulates, resulting in a false, lower concentration. Using SPE disks, the particulates are held on the disk and when the bottle is rinsed the solvent flows through the particulate as well, extracting analytes that may have been held by the particulate, in essence a one-step approach. If the sample is very heavily particulated, a special disk holder (EZ Flow) may be used to allow easy placement of pre-filters and glass wool on top of the SPE disk to further facilitate flow.

Table 1: Recent European Methods using SPE Disks

Method	Title	Status
EN 16691	Water quality – Determination of selected polycyclic aromatic hydrocarbons (PAH) in whole water samples – Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)	Approved 27 June 2015
EN 16693	Water quality – Determination of organochlorine pesticides (OCP) in whole water samples – Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)	Approved 27 June 2015
EN 16694	Water quality – Determination of selected polybrominated diphenyl ether (PDBE) in whole water samples – Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)	Approved 27 June 2015
CEN/TS 16692	Water quality – Determination of tributyltin (TBT) in whole water samples – method using solid phase extraction (SPE) with SPE disks and gas chromatography with triple quadrupole mass spectrometry	1 April 2014, provisional application

Table 2. Extraction Method for PAHs

Step	Solvent	Soak Time	Dry Time
Prewet 1	Methanol	2:00 min	5 sec
Prewet 2	Reagent Water	1:00 min	5 sec
Prewet 3	Reagent Water	30 sec	2 sec
Sample Process			
Air Dry 1:00 min			
Rinse 1	Acetone	2:00 min	2:00 min
Rinse 2	Hexane	2:00 min	2:00 min
Rinse 3	Hexane	1:00 min	1:00 min
Rinse 4	Hexane	1:00 min	1:00 min

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Table 3. Recovery Data of 20 µg PAH Spike with the EZ Flow Disk Holder and 1 Minute Air Dry Times

Compound	Replicate 1 (% Recovery)	Replicate 2 (% Recovery)	Replicate 3 (% Recovery)	Average (% Recovery)	% RSD
Naphthalene	77	78	84	79	4.78
Acenaphthylene	77	85	86	83	5.84
Acenaphthene	82	87	88	85	3.77
Fluorene	79	87	88	85	5.71
Phenanthrene	80	85	87	84	4.32
Anthracene	80	88	87	85	5.13
Fluoranthene	84	88	91	88	4.31
Pyrene	84	89	92	88	4.55
Benz(a)anthracene	85	92	91	89	4.26
Chrysene	83	87	90	86	4.08
Benzo(b)fluoranthene	88	90	90	89	1.49
Benzo(k)fluoranthene	84	90	93	89	5.24
Benzo(a)pyrene	85	91	91	89	3.75
Indeno(1,2,3-cd)pyrene	83	92	93	89	6.17
Dibenz(ah)anthracene	86	94	98	92	6.68
Benzo(ghi)perylene	87	93	96	92	5.01
			Averages	87	4.69

Table 4. Extraction Method for Pesticides

Step	Solvent	Soak Time	Dry Time
Prewet 1	Acetone	1:00 min	1:30 min
Prewet 2	Hexane	1:00 min	2:00 min
Prewet 3	Methanol	30 sec	2 sec
Prewet 4	Reagent Water	10 sec	0 sec
Sample Process			
Air Dry 3:00 min			
Rinse 1	Acetone	3:00 min	2:00 min
Rinse 2	Hexane	3:00 min	2:00 min
Rinse 3	Hexane	1:00 min	1:00 min
Rinse 4	Hexane	1:00 min	1:00 min
Rinse 5	Hexane	1:00 min	1:00 min

Table 5. Organochlorine Pesticide Recoveries

Pesticide Compounds	Concentration (µg/L)	Primary Column CLP 1	Secondary Column CLP 2
		Recovery%	Recovery%
Alpha-BHC	0.50	98	86
Gamma-BHC	0.50	100	88
Beta-BHC	0.50	94	85
Delta-BHC	0.50	100	87
Heptachlor	0.50	91	82
Aldrin	0.50	87	80
Heptachlor Epoxide	0.50	92	82
Gamma-Chlordane	0.50	87	82
Alpha-Chlordane	0.50	91	84
4,4'DDE	1.25	97	85
Endosulfane I	0.50	88	81
Dieldrin	1.25	95	78
Endrin	1.25	92	81
4,4'DDD	1.25	98	86
Endosulfane II	1.25	89	76
DDT	1.25	90	86
Endrin Aldehyde	1.25	90	76
Methoxychlor	5.00	89	81
Endosulfan Sulfate	1.25	94	87
Endrin Ketone	1.25	98	86
Tcmx	1.00	81	76
DCB	1.00	88	76

Next we will discuss two compound classes that can be extracted from more particulated water samples with disk SPE. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants, naturally occurring in coal, crude oil, gasoline, and their byproducts (e.g., coal tar or creosote). In addition, PAHs are formed in the incomplete combustion processes of all organic materials, such as wood or fossil fuels. Consequently, the EU water framework directive (WFD) lists in its annex X the whole group of PAHs as priority hazardous substances and one of the new methods is devoted to these compounds in whole water.

Extraction with DCM is commonly used for PAH compounds, however increasing concern about the health effects of chlorinated solvents has made method developers look for less toxic solvents. Werres, et. al., examined PAH compounds in whole water using acetone as the eluting solvent. (3) However; acetone creates a problem with residual water in the final extracts due to its miscibility with water. The new CEN method specifies elution with DCM and solvent exchange to toluene

SPE-DEX® 4790 Automated Disk Extraction System.

before GC-MS analysis. This work shows SPE using the high-particulate flow holder and elution with hexane as an alternative solvent.(4) Table 2 shows the prewet steps and elution on the SPE-DEX® 4790 automated disk extraction system. The delivery of all steps in the table are completely handled by the 4790 system.

Table 3 shows good recovery for a variety of PAH compounds and good reproducibility with the system set up for higher particulate samples using a non-chlorinated solvent.

Another example of SPE utility is in matching the elution solvent to the needs of the analytical step. Considering the final analytical technique, pesticides are often measured with GC and an electrolytic conductivity detector (ECD) which is specific for organochlorine pesticides and provides a very sensitive measurement. A non-chlorinated solvent is essential for the determinative step to preserve the detector. Exchanging the solvent is a tedious step that can also cause analyte loss. However, it is possible to use a solvent compatible with the detector for elution, eliminating the solvent exchange step entirely, saving time and preserving the analytes. Table 4 shows the extraction method used for 1 L of a water sample. (5)

The recovery of pesticides using this method is shown in Table 5. The primary column results are excellent. The secondary column, used for confirmation, also shows recoveries within the method criteria. Concentrating a 25 mL extract of hexane to a final volume of 5 mL will take approximately 10 minutes with the DryVap® Evaporation System. Including the 10 minute sample run times on the GC/ECD, samples were extracted, concentrated, cleaned, and analyzed within two hours with excellent recoveries.

Conclusion

The European Union has taken the first steps to incorporate disk solid phase extraction as an option in their water sampling and analysis program. These examples show that there are other options to also consider as they move forward to expand disk use and address more complex samples and issues.

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