

Solid phase extraction techniques for drinking water abstraction monitoring and investigation of pollution incidents

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ABSTRACT

Many important organic contaminants present particular analytical difficulties on account of their polarity and water solubility. Performance test data for two of the most promising approaches: solid phase extraction (SPE) and solid phase microextraction (SPME) are presented. SPE, used in a batch mode, offers a potentially powerful tool as a routine screening method. SPME is probably more useful as a technique to be deployed rapidly in an emergency, particularly when gas chromatography mass spectrometry (GC-MS) general survey screening is to be used.

Key words | odour, pollution monitoring, SPE, SPME, taste

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INTRODUCTION

Water treatment works abstracting from rivers can be vulnerable to sudden, episodic contamination from industrial discharges and pollution incidents. Inherent difficulties associated with the detection and monitoring of organic contaminants include the large number and variety of types of organic chemicals that could have potential for causing a pollution incident and the fact that pollution events are often short lived. The latter means that the concentration of the causative substance may have declined to low levels by the time of any response to the incident, making it difficult to identify the cause and source of pollution. This issue is particularly important in the case of a substance that can cause taste and odour problems at concentrations that are low in relation to analytical capabilities. These substances include a range of polar compounds that currently present difficulties in sampling, sample preconcentration and analytical determination.

Recent pollution incidents in the UK, USA and Spain (Preti *et al.* 1993; Ventura *et al.* 1998) illustrate this. In these cases, contamination of source water with relatively soluble polar substances such as: 2-ethyl-5,5'-dimethyl-1,3-dioxane (EDD), 2-butoxyethanol, and 2,2-dimethyl-

1,3-propane-diol; led to contamination of public water supplies and problems of taste and odour. Considerable difficulty was experienced by the relevant authorities in identifying the substances responsible and the source of pollution.

The use of integrating sampling techniques or continuous systems of monitoring has been proposed in order to allow continuous or sequential batch analyses of intake water. Suitable approaches usually incorporate some form of sample preconcentration to allow detection of contaminants at the low concentrations of interest. Among the most important defining properties of the organic chemicals of potential interest in water are:

- Molecular weight—from about 30 to 1200 atomic mass units (e.g. formaldehyde to microcystin).
- Molecular size from a 5 to >100 Å diameter.
- Water solubility from 1×10^{-6} to 1000 mg l^{-1} .
- Concentration range of interest from 1×10^{-6} to 1000 mg l^{-1} .
- Polarity from cationic through essentially non-polar to anionic.

Table 1 | Examples of potential contaminants of interest

Substance	Reason for concern	Log ₁₀ K _{ow} ¹	Solubility (g/100 ml)	Taste/ odour threshold (ng l ⁻¹) [*]	Henry's Law Constant (atm m ⁻³ mole ⁻¹) [†]
Geosmin	Taste/odour—naturally occurring	3.57	0.015	10	3.1 × 10 ⁻⁶
2-Methyl-isoborneol	As above	3.27	0.032	29	8.9 × 10 ⁻⁶
2-Isopropyl-3-methoxypyrazine	As above	2.37	0.069	2	3.1 × 10 ⁻⁶
2,3,6-Trichloroisoanisole	Taste/odour—anthropogenic	4.01	0.003	7	1.3 × 10 ⁻⁴
2-Ethyl-5,5'-dimethyl-1,3-dioxane	As above	1.96	0.17	< 10	9 × 10 ⁻⁵
2-Butoxyethanol	As above	0.57	6.4	< 10	9.8 × 10 ⁻⁸
2,2-Dimethyl-1,3-propane-diol	As above	0.16	8.2	< 10	3.1 × 10 ⁻⁷
1,4-Dioxane	Solvent/taste	-0.32	20		5.9 × 10 ⁻⁶
P-xylene	As above	3.09	0.02		6.5 × 10 ⁻³
Trichlorobenzene	Taste	3.93	0.001		2.2 × 10 ⁻³
Phenol	Taste	1.51	2.6	< 2000	5.5 × 10 ⁻⁷
Cresol	Taste	2.06	0.89		6.2 × 10 ⁻⁷
Naphthalene	Odour	3.17	0.01	25,000	5.3 × 10 ⁻⁴
Atrazine	Herbicide	2.82	0.02	20,000	4.5 × 10 ⁻⁹
Malathion	Insecticide	2.29	0.007		8.4 × 10 ⁻¹⁰

¹K_{ow} is the octanol–water partition coefficient.

^{*}From Keith (1981).

[†]From Meylan & Howard (1991).

- Water/sorbent partition coefficients (log K_{ow}—octanol/water distribution constant) from 2.0 to >6.0.
- Vapour pressure (volatility) from volatile solvents (e.g. acetone) to involatile solutes (e.g. DDT)—indicated by the relevant Henry's Law Constant.

Whilst no single extraction/concentration technique can accommodate chemicals with such a large disparity of properties, it is important to recognise the need for

monitoring techniques with an exceptionally wide scope of application. Some specific examples of substances of interest, including some of marked taste and odour, are listed in Table 1, with their respective physicochemical characteristics.

We have considered the use of several potentially useful techniques, including: equilibrium dialysis, continuous liquid–liquid extraction, fluidised bed sorption, absorption of contaminants on polyurethane foams or on various species of biota, solid phase extraction and solid phase microextraction. The last two techniques seemed to

us to be the most promising. The aim of this paper is to report a preliminary evaluation of these two potentially useful techniques for application in monitoring water quality at treatment works intakes.

SOLID PHASE EXTRACTION (SPE) CARTRIDGES FOR CONTAMINANT SCREENING

SPE has been used widely for many years as a means of extracting organic determinands such as pesticides, PAHs and other priority pollutants from water samples (e.g. Barcelo 1993; Font *et al.* 1993; Walker *et al.* 1993).

SPE cartridges have been proposed as suitable for the preconcentration of both polar or soluble determinands such as phenols and non-polar determinands. Type ENV + Isolute extraction cartridges (Jones Chromatography, Hengoed, UK) were identified as a potentially useful sampling tool for providing quantitative information for a relatively wide range of chemical contaminants. ENV + is a highly cross-linked polystyrene divinylbenzene polymer with a high surface area ($\sim 1100 \text{ m}^2 \text{ g}^{-1}$), narrow particle size distribution and low fines content. Tests were done to assess the utility of these cartridges for general sample screening/preconcentration under non-optimised conditions. Experimental details were: cartridge type: Isolute ENV + 200 mg resin per 6 ml reservoir capacity; solvation: 5 ml methanol, 5 ml deionised water; sample application: 60 ml h^{-1} ; determinand elution: 5 ml 50:50 hexane/acetone.

TEST DESIGN

Borehole water and sewage effluent samples (1 litre) were spiked with a range of potential contaminants at a level of $\sim 50 \mu\text{g l}^{-1}$. Triplicate samples were passed through separate ENV + SPE cartridges at a flow rate of 60 ml hr^{-1} . Samples were pumped both in and out of the cartridges, to avoid overflow, using a peristaltic pump and PVC and silicone pump tubes and connectors. No sample preconditioning, pH adjustment or 'salting-out' were carried out

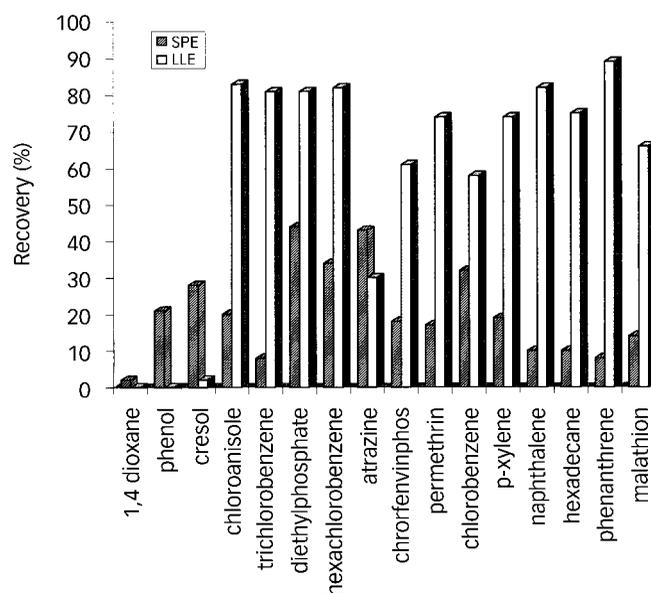


Figure 1 | SPE recovery data compared with liquid/liquid extraction (LLE). Recoveries are from a sewage effluent sample spiked with $50 \mu\text{g l}^{-1}$ of each contaminant.

prior to preconcentration. Solvent eluates were subsequently dried by freezing out residual water and were then submitted for GC-MS analysis. Pesticides were analysed by negative chemical ionisation mass spectrometry, and other determinands by positive ion electron impact mass spectrometry. Quantification was achieved using a range of deuterio-labelled internal standards including: d_3 -1,1,1-trichloroethane, d_6 -benzene, d_5 -phenol, d_{11} -hexanoic acid, d_5 -chlorobenzene, d_{10} -p-xylene, d_{34} -hexadecane, d_{10} -phenanthrene, d_5 -atrazine, d_{10} -malathion. The results for the mean recoveries of contaminants from spiked sewage effluents are shown with corresponding data for liquid/liquid extraction in Figure 1.

It is emphasised that the experimental conditions used here—for column pretreatment, elution solvent, etc.—could be optimised to give better recovery for some determinands, but possibly at the expense of poorer performance for others. The aim was to assess performance for screening purposes, for a range of different types of determinands using a single experimental approach. It was concluded that:

- Preconcentration efficiency does not appear to be simply related to the hydrophobicity of the

contaminant residue. Comparison of $\log K_{ow}$ values with preconcentration efficiency reveals no obvious relationship.

- The preconcentration method has potential for screening for highly soluble contaminants such as phenols and cresols and atrazine, as well as for other more hydrophobic residues. This is a useful characteristic for the qualitative or semi-quantitative screening of samples.
- The approach was not particularly effective for the cyclic ether 1,4-dioxane. This contaminant was chosen to represent a class of high taste/odour substances that pose particularly difficult analytical problems because of their high water and low $\log K_{ow}$ (for 1,4 dioxane: water solubility at 25 °C = 214 g l⁻¹; $\log K_{ow} = -0.32$; [from structure activity relationships (Sabolic 1984)]) which influence extraction efficiencies. Similarly, poor extraction efficiencies were found for 1,4-dioxane using liquid-liquid extraction, though recoveries might be improved somewhat using 'salting out' techniques.

SOLID PHASE MICROEXTRACTION (SPME) FOR CHECKS AT THE TIME OF POLLUTION INCIDENTS

SPME is a rapid, relatively inexpensive, solvent-free extraction method for the isolation of organic contaminants from aqueous solutions at sub micrograms per litre concentration levels. It has been identified as a simple alternative to purge and trap methods used for analysing volatile organic compounds in water samples (Hine & Mookerjee 1975; Shirey 1994; Shirey *et al.* 1995; Whang & Pawliszyn 1998). The technique involves the sorption of organic residues from a water sample onto an optical fibre coated with poly(dimethylsiloxane) polymer. The fibre is immersed in, or held above (Zhang & Pawliszyn 1993) the aqueous sample, then removed, and the organic compounds thermally desorbed into the injection port of a gas chromatograph. Selectivity can be controlled by using different phase coatings or thicknesses. In contrast with SPE, sample conditioning is not required to ensure maximum extraction efficiency. The technique has been used

successfully for the determination of volatile organic compounds such as benzene, toluene, ethylbenzene and xylenes, and for the less volatile polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and the more polar and water soluble phenols. As SPME can be used to preconcentrate determinands over a wide range of concentrations from microgram per litre to milligram per litre levels, it may be adapted for rapid screening of samples.

Two types of solid-phase micro-extraction fibre were obtained (Supelco, Poole, UK), each with a different fibre-coating sorptive phase. Polydimethylsiloxane (PDMS) coated fibres are recommended for extraction of non-polar determinands. Polyacrylate (PA) coated fibres are suitable for the extraction of more polar determinands. Fibres were installed in the fibre assembly and preconditioned by heating in a GC detector at 320 °C for 2 h after which they were ready to be used for extraction purposes. Preconditioning and desorption were carried out using a Perkin Elmer gas chromatograph (8700 GC) fitted with a programme temperature vaporiser (PTV) with a 30 m DB1 column and flame ionisation detector (FID). After sampling, the fibre was desorbed in the GC injector at 300 °C. The GC was programmed as follows: 4 min 50 °C; ramp up at 20 °C min⁻¹ to 140 °C; ramp up at 4 °C min⁻¹ to 200 °C; ramp up to 300 °C at 20 °C min⁻¹. It was accepted that this configuration would not necessarily provide optimum selectivity but it was used to assess general SPME performance for some specific priority contaminants under different conditions.

The rate of SPME fibre equilibration was investigated for a selection of priority contaminants. Fibres were exposed for periods of up to 1.5 h in separate stirred spiked River Thames water samples spiked with 1,2-dimethylnaphthalene (DMN), phenol, atrazine, 1,2,4-trichlorobenzene (TCB) and trichloroethene (TCE) at concentrations of 1 mg l⁻¹. Equilibration was substantially complete within approximately 30 min (see Figure 2). Replicate SPME sorption tests indicated that a relative standard deviation (RSD) of sorption of between 5 and 15% could be achieved for concentrations at the relatively elevated concentration of 1 mg l⁻¹ (Table 2a). The results for SPME performance in stirred and un-stirred samples are shown in Table 2b. These illustrate a

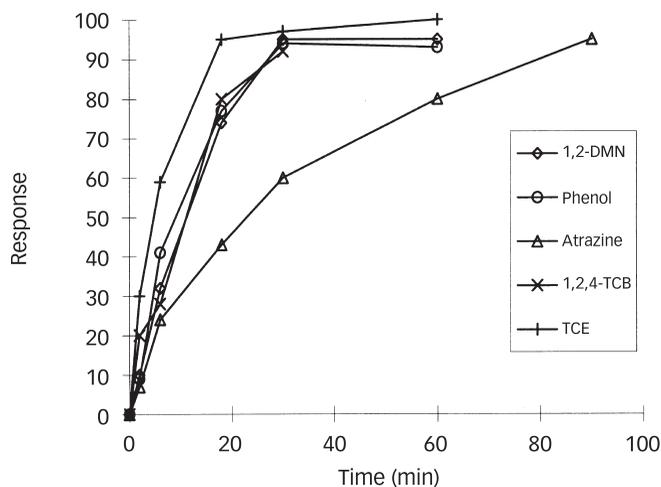


Figure 2 | SPME response versus equilibration time for continuous exposure. Units of response are arbitrary (peak area).

significant reduction in response in unstirred water samples. This effect is probably a result of determinand sorption being diffusion-controlled in the unstirred samples. Levels of DOC had little effect on sorption. The amount of time elapsed prior to analysis of sorbed residues was found to be an important factor as response for volatile contaminants (e.g. trichloroethylene) declined rapidly within an hour of exposure. This is a potentially serious drawback; it means that sample preconcentrates on fibres should be desorbed and analysed within a few minutes after sample exposure.

SPME fibres were assessed for potential use as integrating sampling devices in a simple flow-through system. SPME fibres were inserted below the water surface in a 100 ml cell through which a spiked filtered Thames water sample was introduced at rate of 1 ml min^{-1} via a peristaltic pump. The cell contents were continually stirred and fibres were analysed following the introduction of a short-lived pulse of contaminant (of concentration $1\text{--}4 \text{ mg l}^{-1}$), followed by a return to unspiked 'background' levels for a period of 16 h. Results showed that although the fibres responded to the initial contaminant plume, levels detected on the fibres declined to low or undetectable levels after the exposure to the background sample. The results suggest that desorption of determinands is occurring when contaminant levels in the passing

influent sample decline to background levels. For this reason SPME fibres appear to have limited utility as 'on-line' sentinel monitoring devices. Data in Table 3 illustrate that the use of two different types of SPME fibre can help to address the determination of substances of different types.

It was concluded that:

- SPME fibres appear to have potential for rapid general survey screening for a wide range of organic contaminants that could cause a pollution incident.
- Recoveries of determinands using PA and PDMS fibres show a correlation with hydrophobicity ($\log K_{ow}$).
- SPME fibres can detect a range of contaminants with different physicochemical properties and structures. However, limits of detection could be a serious limitation.
- Results from SPME flow-through tests suggest that considerable desorption of determinands occurs when contaminant levels in a sample stream decline to background levels after a pulse at elevated concentration. Hence, SPME fibres may have limited utility as sentinel monitoring devices. However, SPME could certainly be adopted as a relatively cheap sample screening tool for use in emergencies, if samples are provided in batch form.

CONCLUSIONS

SPE, used in a batch mode, offers a potentially powerful tool as a routine screening method. Two distinct modes of use are possible. In the first, cartridges might be eluted for analysis on a regular routine basis as a means of actively monitoring for potential contaminants. In the second, cartridges might be used to collect samples on a regular basis, stored under refrigeration and analysed only if pollution is indicated/suspected. SPME is probably more useful as a technique to be deployed rapidly in an emergency, particularly when GC-MS general survey screening is to be used.

For both techniques, it is important that the 'background' profiles of contaminants in any given source of

Table 2a | Analytical precision data using SPME

	Response (arbitrary units: GC-MS peak area)				
	1,2-DMN	Phenol	Atrazine	1,2,4-TCB	TCE
Replicate no.					
1	25.9	30.0	27.5	82.7	25.8
2	23.5	33.1	26.1	72.5	22.2
3	28.3	36.2	23.5	74.1	18.6
4	29.0	33.0	30.2	75.2	19.3
5	29.6	35.4	22.6	73.4	
Mean area	27.26	33.54	25.98	75.58	21.5
Standard deviation	2.5	2.4	3.1	4.1	3.3
RSD (%)	9.3	7.2	11.8	5.4	15.3

Table 2b | SPME performance characteristics

	Response (arbitrary units: GC-MS peak area)				
	1,2-DMN ¹	Phenol ²	Atrazine ³	1,2,4-TCB ⁴	TCE ⁵
Stirring effect					
Stirred	43.0	33.5	21.1	73.4	25.8
Unstirred	11.1	29.6	16.3	34.5	15.9
Water type					
Deionised	41.9	33.8	19.7	74.5	35.7
Filtered Thames	35.0	33.5	21.1	73.4	36.2
High DOC	35.5	38.3	22.2	72.7	38.1
Variation between fibres					
Fibre 1	43.0	33.5	26.0	73.4	25.8
Fibre 2	61.8	33.5	24.7	56.5	33.2
Fibre 3	68.6	—	27.5	—	32.8
Flow through cell (1 h/16 h)	24:4	124:ND	—	54:26	—

Note: Tests were performed using PDMS fibres for 1,2-DMN, 1,2,4-TCB and TCE; PA fibres were used for phenol and atrazine tests.

¹1 mg l⁻¹ spike level; ²8 mg l⁻¹ spike level; ³4 mg l⁻¹ spike level; ⁴4 mg l⁻¹ spike level; ⁵20 mg l⁻¹ spike level; ND=not detected.

Table 3 | Theoretical and measured partitioning data for SPME fibres

Compound	Log K_{ow}	Measured log K_d	Solubility (mg l ⁻¹)
Phenol	1.5	2.4 (PA)	87,000
Atrazine	2.3	3.1 (PA)	28
1,2,4-Trichlorobenzene	4.0	3.4 (PDMS)	38
1,2-Dimethylnaphthalene	4.3	3.0 (PDMS)	15
Tetrachloroethylene	2.9	2.6 (PDMS)	150

K_d =fibre/water partition coefficient=concentration of compound on fibre (mg kg⁻¹*)/concentration of compound in water (mg l⁻¹).

*Mass of fibre coating estimated from coating thickness (µm), length/volume of fibre and assuming nominal density of 1 g cm⁻³.

Solubility data predicted using structure activity data (Sabolic 1984).

raw water should be obtained at the outset of monitoring and on a regular basis subsequently. This is essential if the introduction of new contaminants is to be identified. Support information should also include mass spectral data and limits of detection achieved by the monitoring system for specific contaminants (including those identified on the basis of local information as posing a high risk of pollution).

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