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Short communication

Micro versus macro solid phase extraction for monitoring water contaminants: A preliminary study using trihalomethanes

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HIGHLIGHTS

- Traditional and micro solid phase extraction methods were compared.
- Four common disinfection by products were used to assess each method.
- Micro SPE provided better recoveries for all compounds tested than traditional SPE.
- Micro SPE required less sample and less solvent volumes than traditional SPE.
- Micro SPE is underexploited but has a large range of potential application in environmental science.

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ABSTRACT

Solid phase extraction is one of the most commonly used pre-concentration and cleanup steps in environmental science. However, traditional methods need electrically powered pumps, can use large volumes of solvent (if multiple samples are run), and require several hours to filter a sample. Additionally, if the cartridge is open to the air volatile compounds may be lost and sample integrity compromised. In contrast, micro cartridge based solid phase extraction can be completed in less than 2 min by hand, uses only microlitres of solvent and provides comparable concentration factors to established methods. It is also an enclosed system so volatile components are not lost. The sample can also be eluted directly into a detector (e.g. a mass spectrometer) if required. However, the technology is new and has not been much used for environmental analysis. In this study we compare traditional (macro) and the new micro solid phase extraction for the analysis of four common volatile trihalomethanes (trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane). The results demonstrate that micro solid phase extraction is faster and cheaper than traditional methods with similar recovery rates for the target compounds. This method shows potential for further development in a range of applications.

1. Introduction

Solid phase extraction (SPE) is a simple and effective extraction technique for isolating target compounds from aqueous solutions. It utilises a small cartridge packed with solid particle, chromatographic material (sorbent or resin) that acts much like a high performance liquid chromatography (HPLC) phase and which utilises partitioning or distribution processes to chemically separate the different components of a liquid sample (Huck and Bonn, 2000).

SPE was developed in the late 1970s and has been in common use since the mid-1980s (Huck and Bonn, 2000). Since that time it has become one of the most powerful and commonly used sample preparation techniques in analytical and environmental chemistry. It enables researchers to isolate organic analytes from large volumes of water, concentrates trace amounts of contaminants to detectable levels and eliminates much of the glassware and organic solvents necessary with liquid–liquid extraction procedures (Jones et al., 2003). Additionally, by switching from the original environmental matrix to an organic solvent, or ultra pure water, the final analysis is simplified and the demand placed on analytical instrumentation is substantially reduced (Thurman and Mills, 1998).

Traditional, cartridge based systems do have some limitations. Preconcentration of trace levels may require the filtration of large volumes

Abbreviations: SPE, Solid phase extraction; THMs, Trihalomethanes; DBP, Disinfection by-product; HPLC, High-performance liquid chromatography; HAAs, Haloacetic acids; HANs, Haloacetonitriles; HAs, Haloacetaldehydes; HKs, Haloketones; TCM, Trichloromethane; BDCM, Bromodichloromethane; DBCM, Dibromochloromethane; TBM, Tribromomethane; WWTP, Wastewater treatment plant; μECD, Micro-electron capture detector; LLE, Liquid–liquid extraction

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(1 L or more) of water and if they have a high particle load, such samples may take an hour or more to pass through the sorbent bed, which increases the risk of sample degradation (Huck and Bonn, 2000). A vacuum manifold and pump are needed, which means that the systems require electrical power and are not generally portable, meaning that samples must be brought to them, increasing the potential for error. Organic solvents are also required to elute the samples from the sorbent and the cartridges themselves are made of non-biodegradable plastic and are not reusable.

Micro SPE cartridges are a very recent development; the system tested in this study was only brought to market in 2014. These systems utilise sorbents with a very small particle size of 3 μm, compared to 50–60 μm used in traditional SPE, and thus have a greater surface area for sorbtion. The cartridges are handheld, and only need microliters of solvent to condition the sorbent and elute the sample. The cartridges themselves are reusable up to 100 times (with clean samples). The system is also sealed from the external environment so losses of volatile compounds are minimal. Micro SPE therefore offers great potential in a range of applications, especially in the environmental field.

Despite their clear advantages, there are currently very few studies assessing the performance of micro SPE systems. Most of the studies that have been published relate to extracting compounds such as proteins (Tong et al., 1999), cannabinoids (Montesano et al., 2014) or pharmaceuticals (Shen et al., 2006) from biological matrices such as blood or urine. There have also been a few studies looking at contaminants in food (Huang et al., 2012) and wine (Mateo-Vivaracho et al., 2009) but the use of micro SPE in environmental assessment appears to be limited to a paper on assessing the use of one form of the technology for trace cadmium and lead determination, and this required the use of a special PVC adapter rather than a commercial system as used in this research (Anthemidis et al., 2011).

The present study is designed to compare and contrast the performance of traditional and micro SPE cartridges for extracting volatile environmental contaminants. The results are intended to demonstrate the potential of the micro SPE system, primarily for environmental science but potentially also for other fields such as biochemistry and pharmacology.

Four common trihalomethanes disinfection by-products (DBPs) were chosen as test compounds. DBPs are classed as contaminants of emerging concern and may be formed during the chemical disinfection of water (Watson et al., 2012) DBP formation results from addition, oxidation or substitution reactions between the chlorine (or other halogens) and natural organic matter present in the source water (McCormick et al., 2010). The most commonly observed DBPs are the trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloacetaldehydes (HAs) and haloketones (HKs) (Zhang et al., 2004). THMs are the most commonly formed DBPs and were first identified during the chlorination of water in the early 1970s by Rook (1974). Many THMs are toxic and some, such as trichloromethane (TCM) are known carcinogens (Watson et al., 2012). Background levels of these compounds in drinking water are strictly regulated but the increasing use of recycled water in many areas of the world means that the development of new, fast and economical methods for their extraction from a range of aqueous samples is of interest, particularly in countries such as Australia, where water recycling is extensively practised (Williams et al., 2014). This is important since treated wastewater can make up a large proportion of freshwater streams and rivers, particularly in the drier parts of the year and may also be used to water crops and municipal areas such as sports fields. If the recycled water has been chlorinated then DBPs may be present (Sharma et al., 2014). The attenuation rates of recycled water disinfection by-products in a natural reservoir system were recently tested and shown to be quite short, with half-lives ranging from 1.5 to 1.6 days (Williams et al., 2014). However, the continuous input of these compounds may impart a form of pseudo-persistence in the same way as been demonstrated for pharmaceuticals (Richardson and Ternes, 2014). The potential presence of these compounds as emerging contaminants in water analysis and treatment therefore warrants further investigation.

2. Materials and methods

2.1. Chemicals and equipment

All solvents and chemicals were of >98% purity (HPLC Grade). Standards of bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM) were purchased from Sigma-Aldrich (Castle Hill, NSW, Australia) while trichloromethane (TCM) and methanol were purchased from Merck Millipore (Kilsyth, VIC, Australia). The Standard SPE cartridges used were Supelclean™ ENVI-18 (0.5 g/6 mL and 1 g/6 mL, Sigma-Aldrich, Castle Hill, NSW, Australia) and Hypersep™ C-18 (1 g/6 mL, Thermo Fisher Scientific, Scorseby, VIC, Australia) phases. The micro SPE C-18 (3.7 +/− 0.2 mg/8 μL) cartridges were obtained from ePrep Pty Ltd. (Ringwood, VIC, Australia). Whatman filters were obtained from Thermo Fisher Scientific.

2.2. Spiking and recovery studies

Recovery studies were carried out for both the traditional and micro SPE systems using both Milli Q (18.2 M Ω) and Class A recycled water collected from Wastewater Treatment Plants (WWTPs) in western and south-eastern Melbourne. Class A water is defined by Environmental Protection Agency Victoria (2003) as having been treated to a 'fit for purpose' standard for; urban (non-potable) uses with uncontrolled public access; agricultural use e.g. human food crops consumed raw or industrial standard — open systems with worker exposure potential. Recycled water is of particular interest in Australia; this resource is increasingly being used to make up for shortages from other sources and this increases increasing the potential for humans to be exposed to any contaminants contained within it.

Enough water samples were collected to run replicate samples for both forms of extraction. Twelve litres of water was collected for standard SPE but for micro SPE, only around 100 μL was needed per extraction so only a one-litre sample was collected. All samples were left open to the atmosphere for 48 h prior to analysis to ensure all volatile components were removed prior to spiking and all water samples were spiked with standards of each THM at a concentration of 0.1 mg/L.

The water from the WWTP was filtered using first 100 μm and then 0.25 μm Whatman filters to remove particulates before extracting for standard SPE but the micro SPE cartridges did not require filtering before extraction. All primary studies; including extractions used to observe effect of varied flow rates, were run in triplicate. Recovery tests were completed using 9 replicates Milli Q and Wastewater extractions for traditional cartridges (with an extraction time of 120 min) or 12 replicates for the micro SPE system.

2.3. Solid phase extraction

Two forms of a solid phase extraction (SPE) were used to extract the target compounds from the sample matrix as an alternative to methods based on liquid–liquid extractions (LLEs) and Purge and Trap systems (Allard et al., 2012; Pavon et al., 2008). The methods tested were the traditional vacuum manifold based system and the new SPEed® micro cartridge SPE system from ePrep Pty Ltd.

For the standard SPE system the method outlined in Gioia et al. (2004) was used, with the exception that the elution solvent was methanol rather than pentane as the former was found to give better recoveries. Preliminary recovery testing was performed using Supelclean™ ENVI-18 (500 mg/6 mL), Supelclean™ ENVI-18 (1 g/6 mL) and HyperSep™ C-18 (1 g/6 mL) traditional cartridges; both the highest recoveries and most reproducible results were obtained with the C-18 sorbent. The final method involved pre-treatment of the cartridges by activating with 4 mL of acetonitrile, followed by 4 mL of Milli Q water

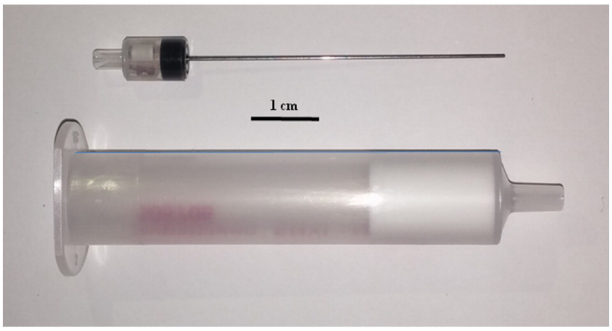

Fig. 1. Photograph showing a standard SPE and the micro SPE cartridges.

(filtered in-house with a 0.25 μm Whatman filter). An aliquot of 100 mL of the filtered sample was then passed through at a flow rate of approximately 0.8 mL/min. The retained THMs were then eluted with 1 mL of methanol and this aliquot was then used for the final analysis.

The ePrep® system is shown in Fig. 1. The dimensions of the sorbent bed were 2.1 mm by 2.3 mm, the bed volume was 8 μL and aspiration flow path volume (needle and valve) was 4 μL. The cartridge incorporates a one-way micro check valve that enables the sample, reagents and solvents to be aspirated directly into the syringe barrel and then allows liquid at high pressure to be directed through the sorbent bed and out of the needle. For the interested reader, further details of the system can be seen at the manufacture's website (ePrep, 2014). As the C18 sorbent had already shown have the best recovery rates for the compounds under study during preliminary testing this sorbent used for the micro SPE system.

The cartridges were used as per the manufacturer's instructions; these were to i) precondition the sorbent with 50 μL of an organic solvent (methanol), ii) condition with 50 μL of ultra pure water, iii) take up 100 μL of sample, iv) wash with 100 μL of water, and then v) to elute with 50 μL of organic solvent. A number of solvents were also tested for their extraction efficiency of the four analytes with the micro cartridges with methanol again found to give the best results (see Table 2). Two,100 μL aliquots of organic solvent were also included as a wash step to ensure the sorbent was clean. These final two aliquots were analysed for THMs in the same way as the sample aliquot to assess if sample carryover occurred. The flow rate was ~100 μL a minute and the cartridges were stored with a solution of 10% methanol/90% water on the sorbent bed when not in use.

2.4. Analytical methods

All extracts were analysed using a modified version of the US EPA method 551 (Hodgeson and Cohen, 1990). Analyses were performed using an Agilent 6890 Series Gas Chromatograph with micro-Electron Capture Detection (μECD). Chromatographic separations were completed using a SGE BP264 column 30 m × 220 μm, 1.2 μm film thickness (SGE Analytical Science, Ringwood, VIC, Australia). Injections of 1 μL were made with a split ratio of 50:1, where the injection port was kept at 220 °C and the detector temperature at 230 °C. The GC oven was set to a temperature programme beginning at 35 °C for 1 min, then heated to 230 °C at 25 °C/min. The total run time was 8 min. The carrier gas used was H_2, flowing at a constant rate of 1.6 mL/min which resulted in the following elution times, TCM = 3.18 min, BDCM = 4.08 min, DBCM = 4.95 min and TBM = 5.77 min.

To ensure the correct identification and quantification, three control criteria were used:

1. The observed retention times (within ± 0.1 min) were required to match the times found when identifying the analyte peaks with the use of standard solutions.
2. The signal-to-noise ratios for all quantified peaks were required to be greater than 10:1.
3. The extraction recoveries were required to be reproducible for three sets of triplicate samples.

All wastewater sample runs were completed with both laboratory blanks and spiked blanks, to ensure that constant recoveries were being achieved for each extraction undertaken. Laboratory blanks were also tested after every 20 samples. No signals were detected in these samples.

3. Results and discussion

3.1. Recoveries

The maximum recoveries achieved for the four THMs in spiked samples of Milli Q water and wastewater are shown in Table 2. It can been seen that the micro SPE system gives substantially better recoveries than the traditional SPE method for three of the compounds (TCM, TBM and BDCM) and comparable results for the remaining one (DBCM) in the Milli-Q water. Lower recoveries for both types of SPE were observed when using the spiked wastewater but the micro SPE system still substantially outperformed the traditional system for this matrix.

The spiking levels of 100 ppb used in the recovery testing were chosen to ensure all analyte peaks were well above the limit of quantification (defined as a 10× the signal to noise ratio) and this was successful. Indeed, obtaining half the signal response observed, or even a 10th would still have given useable data. It would also have been possible to pass more extractions of water through on the same micro cartridge to increase the amount of analyst sorbed to boost the recovery of compounds present at lower concentrations if needed.

All recoveries were slightly lower than those reported for liquid–liquid extraction, 78% (DBCM) to 138.4% (TCM) and purge and trap analysis; 86% (TCM) to 124% (BDCM) (Nikolaou et al., 2002). However, the results obtained in the present study were high enough for use, as well as being reproducible (see Tables 1 and 2). Both SPE systems required minimal use of solvents and glassware. The micro SPE system was also much faster (<2 min compared to over 2 h) and used microliters of solvent compared to millilitres for the traditional SPE system.

Table 1
Recoveries of each THM using the micro SPE system and eluting with selected solvents.

Cartridge	Sample matrix	Extraction time	Solvent	Sample volume	Eluted volume	Recovery %			
						TCM	BDCM	DBCM	TBM
Supelclean™ ENVI-18 0.5 g/6 mL	Pure	10 min	Methanol	100 mL	10 mL	2 ± 14	10 ± 15	33 ± 16	46 ± 15
Supelclean™ ENVI-18 0.5 g/6 mL	Pure	66 min	Methanol	100 mL	10 mL	12 ± 6	22 ± 8	40 ± 10	47 ± 12
Supelclean™ ENVI-18 0.5 g/6 mL	Pure	135 min	Methanol	100 mL	10 mL	17 ± 7	27 ± 11	45 ± 14	74 ± 14
Supelclean™ ENVI-18 1 g/6 mL	Pure	120 min	Methanol	100 mL	10 mL	33 ± 2	53 ± 4	67 ± 6	74 ± 8
HyperSep™ C-18 1 g/6 mL	Pure	120 min	Methanol	100 mL	10 mL	30 ± 11	50 ± 12	72 ± 12	82 ± 11
HyperSep™ C-18 1 g/6 mL	Pure	120 min	Methanol	100 mL	1 mL	24 ± 23	36 ± 23	38 ± 22	33 ± 21
HyperSep™ C-18 1 g/6 mL	Wastewater	120 min	Methanol	100 mL	1 mL	11 ± 13	21 ± 13	26 ± 13	24 ± 12
ePrep SPEed© C-18 3.7 ± 0.2 mg/8 μL	Pure	<2 min	Methanol	100 μL	50 μL	50 ± 7	72 ± 8	63 ± 10	83 ± 15
ePrep SPEed© C-18 3.7 ± 0.2 mg/8 μL	Wastewater	<2 min	Methanol	100 μL	50 μL	39 ± 20	54 ± 10	58 ± 10	55 ± 17

Table 2
Comparison of the percentage recovery of each THM with the various forms of SPE assessed.

Solvent	Sample type	Average recovery % ± % RSD				Pre-concentration
		TCM	BDCM	DBCM	TBM	
Methanol	Milli Q	50 ± 7	72 ± 8	63 ± 10	83 ± 14	2×
Methanol	Wastewater	39 ± 20	54 ± 10	58 ± 10	55 ± 17	2×
Acetonitrile	Milli Q	52 ± 15	70 ± 15	73 ± 18	64 ± 19	2×
Acetonitrile	Wastewater	48 ± 18	54 ± 13	41 ± 18	27 ± 27	2×
Acetone	Milli Q	41 ± 7	72 ± 8	46 ± 8	68 ± 8	2×
Iso-propyl alcohol	Milli Q	47 ± 34	87 ± 35	56 ± 34	85 ± 34	2×

3.2. Sample carry-over

Standard SPE cartridges are one-use only and are thrown away after the elution step. This is both uneconomical (as the cartridge has to be replaced) and environmentally unfriendly as SPE cartridges are plastic and do not break down quickly in landfill. In contrast, micro SPE cartridges are designed like small HPLC columns and are thus marketed as being reusable. As described in Section 2.3 this was tested by running three, 100 μL volumes of methanol through each cartridge after eluting the sample. The results of this can be seen in Fig. 2. It can be seen that while sample carry over from the elution step to the first and second wash steps is minimal, it does occur and so it is important to include at least three wash steps after each sample has been eluted. In addition, when extracting from wastewater the cartridge became visibly dirty after 12 uses (a thick black line appeared above the sorbent bed), although in these 12 extractions there was no change in recovery rates.

The results of this study show that the micro SPE cartridges are superior to the traditional SPE system in every way for the analysis of THMs. Micro SPE cartridges utilise a much smaller particle size (3 μm compared to 50 μm for normal SPE) and this appears to offer a much more efficient separation of compounds of interest from the interfering matrix. The resulting increase in resolution enables similar or better recovery rates to be obtained than with traditional SPE but with the use of much less sample and solvent (μL rather than mL or L). The cartridges are also reusable, thus extending their working life.

4. Conclusions

This study has shown that micro solid phase extraction can provide an innovative method of detection of THMs that is faster, cheaper and greener than traditional methods. Since the micro SPE system could potentially be used in any study where solid phase extraction is needed there is a wide scope for the development of a wide range of sample preparation applications in the hydrosphere, biosphere, and atmosphere and to greatly influence environmental and analytical chemistry.

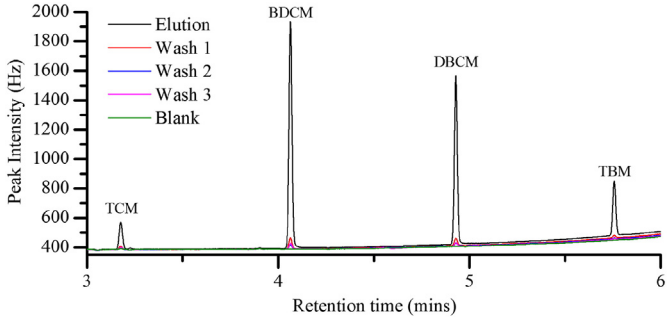

Fig. 2. GC–ECD chromatograph of Milli Q water spiked with 0.1 mg/L of each compound showing the retention time of the four THMs analysed in the elution step as well as the first two wash steps and a blank.

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