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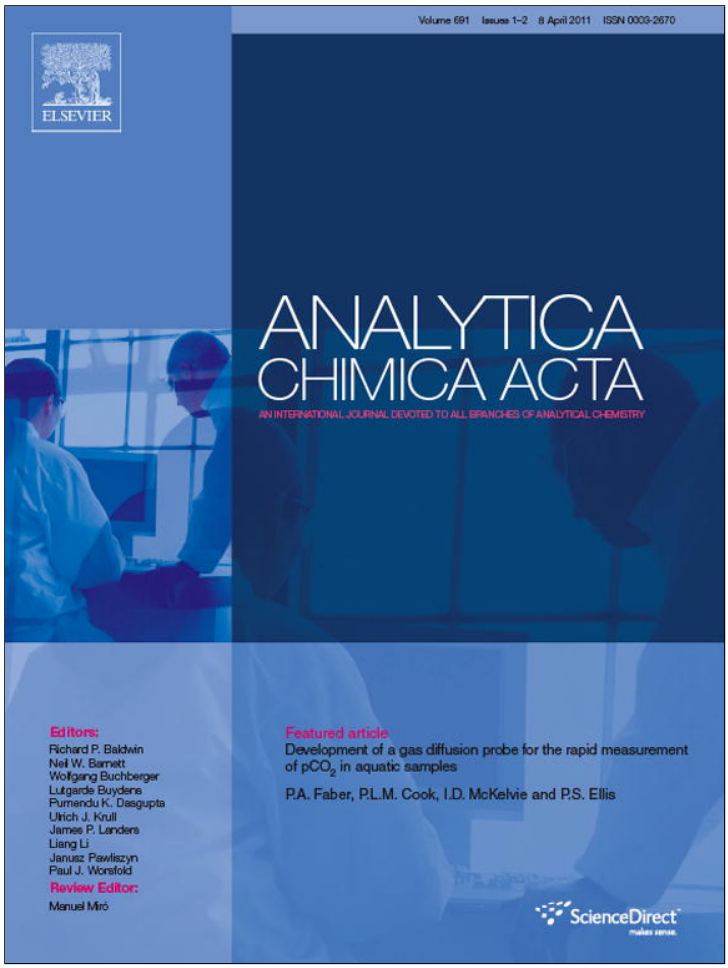

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Fast screening of perfluorooctane sulfonate in water using vortex-assisted liquid–liquid microextraction coupled to liquid chromatography–mass spectrometry

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ABSTRACT

Fast screening of trace amounts of the perfluorooctane sulfonate anion (PFOS) in water samples was performed following a simple, fast and efficient sample preparation procedure based on vortex-assisted liquid–liquid microextraction (VALLME) prior to liquid chromatography–mass spectrometry. VALLME initially uses vortex agitation, a mild emulsification procedure to disperse microvolumes of octanol, a low density extractant solvent, in the aqueous sample. Microextraction under equilibrium conditions is thus achieved within few minutes. Subsequently, centrifugation separates the two phases and restores the initial microdrop shape of the octanol acceptor phase, which can be collected and used for liquid chromatography–single quadrupole mass spectrometry analysis. Several experimental parameters were controlled and the optimum conditions found were: 50 μL of octanol as the extractant phase; 20 mL aqueous donor samples (pH = 2); a 2 min vortex extraction time with the vortex agitator set at a 2500 rpm rotational speed; no ionic strength adjustment. Centrifugation for 2 min at 3500 rpm yielded separation of the two phases throughout this study. Enhanced extraction efficiencies were observed at low pH which was likely due to enhanced electrostatic interaction between the negatively PFOS molecules and the positively charged octanol/water interface. The effect of pH was reduced in the presence of sodium chloride, likely due to electrical double layer compression. The linear response range for PFOS was from 5 to 500 ng L^{-1} (coefficient of determination, r^2, 0.997) and the relative standard deviation for aqueous solutions containing 10 and 500 ng L^{-1} PFOS were 7.4% and 6.5%, respectively. The limit of detection was 1.6 ng L^{-1} with an enrichment factor of approximately 250. Analysis of spiked tap, river and well water samples revealed that matrix did not affect extraction.

1. Introduction

Perfluorinated compounds (PFCs), including perfluoroalkyl sulfonates ($F(CF_2)_nSO_3^-$) and perfluoroalkyl carboxylates ($F(CF_2)_nCO_2^-$) are used on a regular basis for a wide variety of applications, such as water-proofing of materials, protective coating of metals, fire-fighting foams for electrical and grease fires, semi-conductor etching and in lubrication. This is due to their favorable physicochemical properties, which include chemical inertness, low coefficients of friction and low polarizabilities, also known as fluorophilicity [1]. However, the same properties that made PFCs so valuable as commercial products also pose potential drawbacks, including environmental persistence and resistance to conventional remediation or waste treatment technologies [1,2]. The widespread occurrence in environmental and biological samples, including human samples, or even from remote regions such as the Arctic, has drawn considerable interest from the public and regulatory agencies. Pressure is forcing major producers to voluntarily discontinue the production of the most bio-accumulative PFCs, such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which have been categorized as persistent organic pollutants [2–6].

Trace analysis of PFCs has progressed considerably thanks to the introduction of high performance liquid chromatography (HPLC), coupled to different types of mass spectrometers (MS) and research results have been reviewed on several occasions [6–8]. The quantitative determination of PFCs in environmental matrices has been dominated by the use of HPLC-negative electrospray ionization-triple-quadrupole MS–MS [9]. Monitoring transition from parent

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to daughter ion (more selective) was found capable of alleviating matrix interferences during analyte determination in many cases [8,9]. Nonetheless, the high purchase and maintenance costs limit availability for routine analyses [10]. LC with single-quadrupole MS is also considered a sensitive technique, however, effective clean up is recommended especially for PFOS where known matrix interference exists [7,9].

In general, when low concentrations of perfluoroalkyl substances are to be determined, a sample pretreatment step is commonly included in the analytical procedure [6]. Solid-phase extraction (SPE) has become the most popular sample preparation method due to the inherent advantages of high preconcentration factors, low consumption of organic solvents and ease of operation [6–8]. Nonetheless, problems associated with these otherwise multi-step SPE protocols include early breakthrough of water-soluble analytes for C_{18}-bonded silica, high standard deviations, irreversible adsorption for graphitized carbon black [11] and sample contamination during sample handling [7,12,13]. In view of these limitations different alternatives have been published in the literature, such as preconcentration using liquid–liquid extraction [14], large-volume injection of the samples [15,16] or even in-tube solid-phase microextraction (SPME) [17].

Recently, we developed a new fast microextraction method, termed vortex-assisted liquid–liquid microextraction (VALLME), whereby microvolumes of a low-density extractant organic solvent are dispersed into an aqueous sample using vortex mixing, a mild emulsification procedure [18]. The fine droplets formed can extract target analytes towards equilibrium faster because of the shorter diffusion distance and larger specific surface area. Upon centrifugation the extractant acceptor phase restores its initial single microdrop shape in the upper surface of the aqueous solution and can be used for high-performance liquid chromatographic analysis. The objective of this study was to develop a simple and fast analytical method for trace level determination of perfluorosulfonates in water samples based on VALLME and coupled to high performance liquid chromatography–single quadrupole mass spectrometry. For the purpose of the present study, PFOS was chosen as the model analyte, as it is the most commonly occurring contaminant. The parameters, which were controlled and studied in order to evaluate method performance, are given in detail in the following sections.

2. Experimental

2.1. Chemicals and samples

Perfluorooctane sulfonic acid potassium salt (PFOS-K^+; OEKANAL®, analytical standard) and ammonium acetate were purchased from Fluka (Bucks, Switzerland) and Sigma–Aldrich (Steinheim, Germany), respectively. 1-octanol and methanol (Chromasolv LC–MS) were obtained from Riedel-de Haën (Seelze, Germany). When stated in the text, sulfuric acid (Sigma–Aldrich) and sodium hydroxide (Merck, Darmstadt, Germany) were used to adjust the pH and sodium chloride (Merck, Darmstadt, Germany) was used to adjust the ionic strength of the aqueous samples. Aqueous solutions were prepared with purified water from an EASYpure RF system supplied by Barnstead/Thermolyne Corporation (Dubuque, IO, USA). Aqueous working standards were prepared from a methanolic stock solution containing 10 mg L^{-1} of PFOS.

A 100 μL Hamilton (Bellefonte, PA, USA) HPLC 710 SNR model microsyringe was used to inject the organic solvent into the aqueous sample and then collect it for LC–MS analysis.

Recovery studies were carried out using tap water from the Chania (Crete, Greece) water distribution network, river-water samples collected from the Koiliaris River, located in Chania, and a well water obtained from a well in Chania. All samples were collected in polypropylene containers the day before analysis and were stored in the dark at 4 °C.

2.2. VALLME

The general experimental procedure for VALLME was as follows: A 20 mL aqueous sample, with the pH adjusted to two (pH = 2) and spiked with PFOS at a known concentration, was placed in a round-bottom centrifuge glass vial (diameter: ~2 cm). The use of a glass surface has been found not to interfere with the extraction procedure [6,8,19]. For extraction, 50 μL of octanol (the low density solvent acting as the acceptor phase) was slowly introduced and the mixture was vigorously shaken using a vortex agitator from Reax Control (Heidolph, Germany) for 2 min at 2500 rpm (maximum setting) leading to the formation of fine droplets. The two phases were separated by centrifuging the mixture at 3500 rpm for 2 min with a Heraeus Labofuge 400 centrifuge from Kendro Laboratory Products (Langenselbold, Germany). The octanol phase could thus restore its initial single microdrop shape on the upper surface of the sample solution and 30 μL could be collected with the help of a microsyringe and used for LC–MS analysis. During optimization, all experiments were run at least in duplicate.

2.3. LC–MS analysis

The 30 μL octanol extracts were added in 100 μL polypropylene inserts placed in 2 mL polypropylene autosampler vials, equipped with caps from Agilent (Palo Alto, CA, USA). Then, 10 μL were injected onto an Agilent 1200 LC for separation in a Thermo-Electron Betasil C18 column (Waltham, MA, USA) of dimensions 2.1 mm ID, 100 mm length and 5 μm particle size kept at 40 °C throughout analysis. A 1 mM aqueous ammonium acetate:methanol mobile phase was used at a flow rate of 0.20 mL min^{-1}, with an initial composition of 60:40 aqueous:methanol. The LC method used here was based on a previous report and optimized. It consisted of an initial ramp to 40:60 over the first 2 min, then ramping to 10:90 over the next 10 min, followed by a 2 min ramp to 60:40 where it was held for 4 min to allow pressure equilibration. An Agilent 6100 Series Quadrupole LC/MS system with the multimode source operating in the negative electrospray mode was used to monitor the perfluorooctane sulfonate molecular ion. The optimized instrumental conditions were 30 psi for the nebulizer gas pressure, drying gas flow rate and temperature were 12 L min^{-1} and 350 °C for the nitrogen nebulizer gas temperature, the capillary voltage was set at 3500 V and the fragmentor voltage at 140 V. The selected negative-ion mode monitoring of the parent ion for PFOS m/z 499 ($C_8F_{17}SO_3^-$) was used for monitoring and quantification.

The risk of secondary contamination during sample handling and analysis is a major concern in PFCs analysis, given that contamination sources in the laboratory are not well characterised but presumably are numerous [8,9,12,13]. One known source of procedural contamination is fluoropolymers, such as polytetrafluoroethylene or perfluoroalkoxy compounds, which are present in a variety of laboratory products and contribute to background contamination in analytical blanks. Moreover, laboratory materials made of, or containing such compounds were excluded from the extraction step [12]. In addition the scrupulous control of the cleanliness of solutions and glassware aimed minimising the risk of contamination. Despite all precautions taken, the target fluorinated compound is present in a variety of laboratory products and a procedural blank contamination of low concentration and variability was recorded when deionised water was submitted to the proposed VALLME procedure. We therefore tested several procedural blanks

in order to establish the lower quantitation limit for PFOS which was set at 5 ng L^{-1}. Blank subtraction was obviously relevant for low-concentrated samples [13]. It should be mentioned here that PFOA is typically reported as the most abundant laboratory contaminant when compared to PFOS [12,13]. Overall, procedural blanks, as well as octanol blanks, were routinely run to ensure minimum contamination.

3. Results and discussion

3.1. Preliminary experiments

In general, the lack of accurate information on the physicochemical properties of PFCs makes prediction of their fate (and transport) a difficult task [20]. Fluorinated tails (which are both oleophobic and hydrophobic) together with the presence (in most cases) of an anionic functional group (such as the sulphonate in PFOS) affords them moderate to high surface activity, causing them to migrate to the interface of solutions. In a previous study, when PFOS was added to octanol and water in a standard test system, three layers were formed. It was the surface-active properties of PFOS that typically lead to such inseparable emulsions making impossible the direct measurement of the octanol–water partition (K_{ow}) coefficient [20,21]. Preliminary research into different spiked aqueous concentrations of the target analytes, without pH adjustment, revealed that concentrations well above 500 ng L^{-1} are to be avoided as they typically lead to the formation of stable emulsions. Nonetheless, such concentrations are not considered environmentally relevant.

3.2. Optimization of VALLME

Initially, several water immiscible solvents with a density lower than that of water were tested. Each time, a 50 μL microdrop of 1-octanol, toluene, *n*-hexane, octane or decane was slowly introduced on the top surface of the aqueous sample of a 20 mL aqueous sample spiked at 500 ng L^{-1} with the PFOS anion. Dispersion of the organic microdrop into the aqueous phase was achieved using vortex agitation (2 min; 2500 rpm), a mild emulsification process. Subsequent centrifugation (2 min at 3500 rpm) aimed separating the two phases of this liquid–liquid dispersion. From all examined solvents, 1-octanol was the only solvent that could restore its initial single microdrop shape upon centrifugation and could be thus collected and used for analysis. The rest of the tested solvents were left scattered on the top surface of the aqueous solution hindering thus their collection. The above observation is in accordance with our previous report, suggesting once again that the complex mechanisms involved during drop breakage and formation are greatly influenced among others by the physicochemical properties of the two immiscible phases involved [18]. Based on the above 1-octanol was selected as the extraction solvent.

In the case of acidic compounds, lowering the pH is expected to shift the acid/base equilibrium towards the protonated form which has a greater affinity for the relatively non-polar organic phase, thus enhancing extraction [14]. Present knowledge corroborates the idea that PFOS will not protonate significantly at nanomolar concentrations above pH ~ 1, given that its conjugated perfluorooctane sulfonic acid (PFOSA) is a strong acid (pKa < 1) [22]. In fact with a calculated pKa value of around −3 [21], PFOS is expected to carry a negatively charged site at its sulfonate head group under all environmentally relevant pHs. Based on the above, in a separate set of experiments the extraction efficiency of VALLME was investigated as a function of the pH and the results are depicted in Fig. 1. As can be seen increasing the pH of the sample solution from 2 to 9 had an important negative effect on the extraction efficiency of the proposed method. In general, water interfaces with hydrophobic media (such as organic droplets, solid hydrophobic polymers, hydrophobic assembled structures, or even gas bubbles) are usually negatively charged and become positively charged in highly acidic solutions [23]. These charges are created by the preferential adsorption of OH^- or H_3O^+ ions (which are always present in water) at the interface, forming electrical double layers e.g., around organic drops [24]. During the present investigations the fine octanol droplets formed during vortex agitation at higher solution pHs, are expected to be negatively charged due to OH^- adsorption at the water/hydrophobic interface [24–26]. The electrostatic repulsion between the anionic PFOS molecules and the octanol/water interface is thus more likely responsible for the observed reduced extraction of PFOS under high pH values. In general, the preferential adsorption of hydroxide ions at the interface was found to predominate as compared to the adsorption of hydronium ions (H_3O^+) even at similar concentrations, i.e., in solutions of neutral pH [23] given that H_3O^+ ions, being large and hydrated, are kept away from the interface more than the OH^- ions [23,24]. As a result, many reports assign a negative charge at the interface even of pure water, although this is currently under debate in the case of water/vapor interfaces [27,28]. On the other hand the enhanced extraction efficiencies for PFOS observed at lower pH values point towards the positive role of increased hydronium ions at the interface which is now expected to be positively charged [25]. This resulted in an enhanced electrostatic attraction between the negatively charged PFOS molecules and the water/octanol interface [29] promoting thus PFOS adsorption and consequently mass transfer into the octanol phase. The present results are in agreement with previous reports investigating the effect of solution chemistry on the PFOS partitioning at different interfaces, where lowering the solution pH was found to promote PFOS adsorption onto a goethite surface [29] and at the water/bubble interface formed during sonication of aqueous solutions [30]. Based on the above, it was concluded that keeping the pH of the aqueous samples low (pH = 2) for all subsequent experiments would be beneficial for extraction.

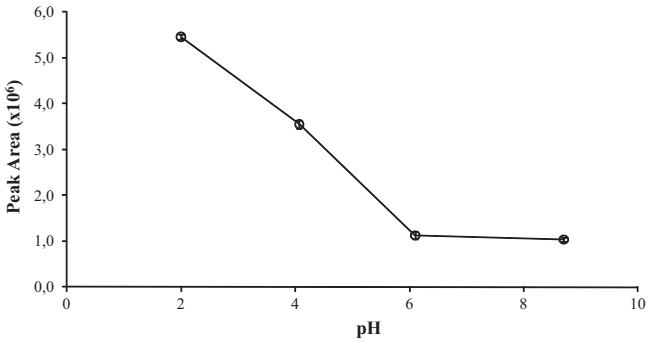

Fig. 1. pH effect upon VALLME. Other experimental conditions: 50 μL octanol, 20 mL aqueous samples spiked at 500 ng L^{-1} with PFOS, 2 min vortex extraction time, vortex agitator set at 2500 rpm rotational speed, and centrifugation for 2 min at 3500 rpm.

The effect of vortex extraction time upon VALLME was then investigated. Fig. 2 depicts the response of the analytical instrument as a function of extraction time. At "0 min", the water–octanol mixtures were directly centrifuged for 2 min at 3500 rpm and the target analyte was extracted solely due to diffusion during this step [31]. Fig. 2 clearly shows that after agitating the mixture for 2 min, the concentration of PFOS in the octanol extract reached equilibrium. It appears that the fine droplets formed during the proposed microextraction procedure were able to extract the target analyte towards equilibrium faster because of the shorter diffusion distance and larger specific surface area [18,32]. Based on the above observation, a 2 min vortex extraction time was chosen as optimum

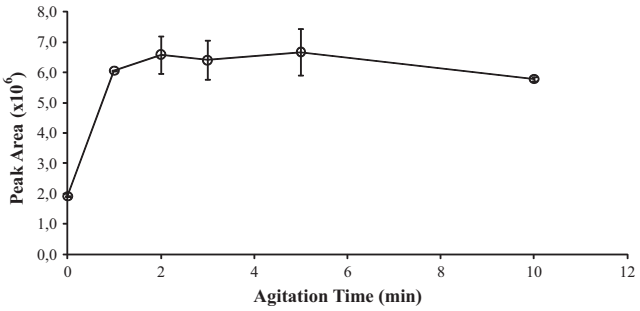

Fig. 2. Effect of vortex extraction time upon VALLME. Other experimental conditions: 50 μL octanol, 20 mL aqueous samples spiked at 500 ng L^{-1} with PFOS; pH = 2; vortex agitator set at 2500 rpm rotational speed, and centrifugation for 2 min at 3500 rpm.

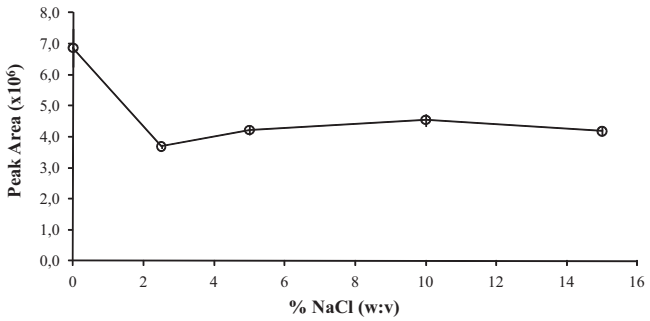

Fig. 3. Effect of ionic strength (% NaCl w:v) upon VALLME. Other experimental conditions: 50 μL octanol, 20 mL aqueous samples spiked at 500 ng L^{-1} with PFOS, pH = 2, 2 min vortex extraction time; vortex agitator set at 2500 rpm rotational speed, and centrifugation for 2 min at 3500 rpm.

for this experimental parameter, thus enabling extraction under equilibrium conditions.

In general, increasing the volume of the sample increases the total mass of analytes available for extraction, thereby enhancing extraction and improving method sensitivity [33]. The present study investigated the effect of aqueous sample volume upon extraction. The volumes ranged from 5 mL to 20 mL (four points) based on the glass vial used and the resulting sensitivity of the method [18]. Overall, extraction of PFOS was approximately 4.3 times larger for 20 mL sample volumes when compared to the 5 mL ones. Based on the above, 20 mL aqueous samples were used for extraction.

A separate set of experiments investigated the effect of octanol volume upon extraction. Accordingly, 20 mL sample volumes containing 500 ng L^{-1} of PFOS at a pH = 2 were extracted using the VALLME procedure with octanol volumes ranging between 50 and 80 μL (four points). In general, increasing the volume of the acceptor phase is expected to decrease enrichment factor and consequently the final concentration of the target analyte in the extractant phase [32]. Provided that each time 30 μL of octanol were collected and used for analysis, a 34% decrease in instrument response was recorded whilst increasing the acceptor phase volume from 50 to 80 μL, reflecting the decrease in the final concentration of target analyte in the octanol phase. Based on the above, 50 μL of octanol was chosen for all subsequent experiments.

In general, depending on the nature of target analytes, addition of salt to the solution can decrease solubility due to the salting-out effect [34]. In the case of PFCs, a salting-out effect was reported in natural waters containing high amounts of dissolved solids. In such matrices, the dissociated anionic PFCs formed strong ion pairs with existing cations [20], increasing thus their chemical hydrophobicity due to neutralisation of the charged moiety [35]. Based on these observations, a final set of optimization experiments investigated the effect of ionic strength upon extraction. Each time, 20 mL aqueous solutions, spiked at 500 ng L^{-1} with PFOS at pH = 2 and a salt content ranging from 0 to 15% (w:v) NaCl, were extracted using VALLME. As can be seen (Fig. 3), the presence of a background electrolyte was found to restrict PFOS extraction. It appears that increasing the ionic strength tends to screen the initial electrostatic attraction between the negatively charged PFOS molecules and the positively charged water/octanol interface due to electrical double layer compression [29]. The effect of pH was thus less significant in the presence of salt and reduced PFOS extractions were recorded. Similarly, high background electrolyte concentration was found to suppress the otherwise positive pH effect on PFOS adsorption onto a goethite surface [29] and the bubble/water interface formed during sonication of an aqueous solution [30]. Based on the above, it was decided not to alter the ionic strength of the aqueous samples prior to VALLME extraction.

3.3. Analytical performance of VALLME

The performance of the proposed method was evaluated using six concentration levels ranging from 5 to 500 ng L^{-1}. Standards were extracted under the optimised experimental conditions (50 μL octanol; 20 mL aqueous working standards; pH = 2; 2 min agitation using a vortex agitator set at 2500 rpm) followed by centrifugation for 2 min at 3500 rpm. The calculated calibration curve

Table 1
Performance comparison of VALLME with other published analytical procedures.

Analytical method	Calibration (ng L^{-1})	LOD (ng L^{-1})	Sample volume (mL)	Reference
VALLME–LC–MS	5–500	1.6	20	This work
LLE–LC–MS–MS	0–50	0.26	900	[14]
SPE–LC–MS–MS	2–20,000	0.1[a]	100	[36]
SPE–LC–MS–MS	10–10,000	0.1	400	[37]
SPE–LC–MS–MS	1–500	0.2	500	[38]
SPE–LC–MS–MS[b]	0.5–20	0.2	500	[11]
SPE–LC–ion trap MS	2–100[c]	0.2	250	[39]
SPE–LC–MS–MS	1–100	2	100	[40]
SPE–LC–MS	100–100,000	0.1	1000	[10]
Large volume injection-LC–MS–MS	25–125	0.5[d]	0.5[e]	[15]
SPE–LC–MS–MS	10–10,000	5	40	[41]
In-tube-SPME–LC–MS	50–5000	3.2	20 × 0.040[f]	[17]

[a] Instrumental LOD in pg when 1L sample is used for extraction.
[b] Mixed hemimicelle-based SPE.
[c] Equivalent linear range for a 250-fold concentration.
[d] Limit of quantification (LOQ).
[e] Wastewater sample.
[f] 20 cycles of 40 μL.

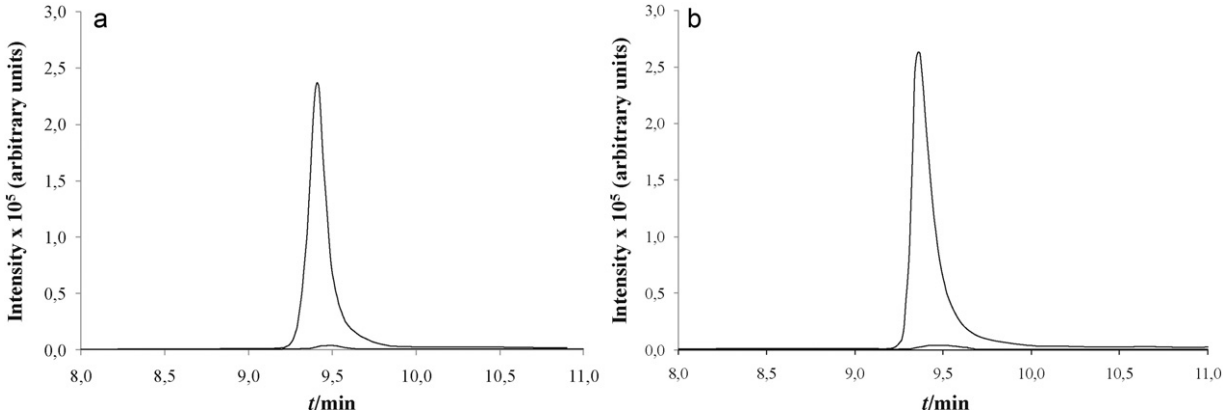

Fig. 4. Superimposed LC–MS chromatograms obtained in the SIM mode (m/z 499) after using VALLME for the extraction of (a) spiked (100 ng L^{-1}) and unspiked (procedural blank) deionised water samples, and (b) spiked (100 ng L^{-1}) and unspiked well water samples.

yielded a high level of linearity yielding a 0.997 coefficient of determination (r^2). The limit of detection (LOD) defined for a signal-to-noise ratio of three (S/N = 3) was found to be 1.6 ng L^{-1} after blank subtraction. The relevant limit of quantification (LOQ), calculated as the S/N = 10, was 5.3 ng L^{-1}. It is important to note that the linear range found here is similar to that obtained when using other sample preparation methods such as liquid–liquid extraction (LLE) or SPE and/or more expensive instrumentation (e.g., LC–MS–MS). The performance of recently published analytical procedures is summarized in Table 1 for comparative purposes.

In addition, method repeatability, expressed as relative standard deviation (RSD), was evaluated after extracting five consecutive aqueous samples at two different concentration levels. During the present investigations, the RSD values of the proposed protocol were 7.4% and 6.5% for 10 and 500 ng L^{-1} contamination levels, respectively. The enrichment factor defined as the ratio between the final analyte concentration in the organic acceptor phase and the initial aqueous sample concentration was found to be approximately 250, demonstrating the high extraction efficiency of the proposed VALLME procedure under the present experimental conditions.

Based on our previous experience, the composition of the sample matrix may affect the extraction efficiency of the proposed method, thus outweighing the advantages of this simple and fast sample preparation method [18]. Therefore, the effect of matrix upon VALLME was evaluated in tap, well and river water samples. Initial investigations consisted of submitting the unspiked real samples to the proposed VALLME method. The PFOS contamination recorded in these samples did not differ substantially from procedural blank contamination and it was concluded that the presence of PFOS was below the limit of quantification (5.3 ng L^{-1}) of the proposed method. Fig. 4 compares typical LC–MS chromatograms obtained after extracting spiked (100 ng L^{-1}) and unspiked (procedural blank) deionised water samples as well as spiked (100 ng L^{-1}) and unspiked well water samples. Recoveries were calculated by relating the amount of analyte found in real samples to that in deionised water solutions (all spiked at 100 ng L^{-1}), after extracting the samples with the proposed procedure (n = 5). The ratios found were expressed as percentages and were 90.8% for tap water (1.0% RSD), 105.1% for well water (4.8% RSD) and 95.5% for river water (9.9% RSD). This demonstrates that the matrices under consideration hardly affected extraction.

4. Conclusions

A new sample preparation method, based on VALLME, has been successfully developed for the fast screening of trace amounts of PFOS in water samples. The proposed analytical procedure does not require the use of certain sample preparation apparatus, which has been repeatedly reported to act as a source of procedural contamination or uncertainty. Several factors that influence extraction efficiency have been investigated. The high enrichment factor found in this study demonstrates the excellent extraction efficiency of the proposed sample preparation method. Given its simplicity and resulting sensitivity, this method can be recommended for the fast screening of PFOS in relatively simple environmental aqueous matrices.

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