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Smartphone-based / Fluoro-SPE for selective detection of PFAS at ppb level

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ABSTRACT

Fluoro-solid phase extraction (fluoro-SPE) has been well established to selectively extract targets after they have been fluoro-tagged. Here we report that this technique can also be used to selectively extract fluorosurfactants of PFAS (per- and poly-fluoroakyl substances), which have fluoro-carbon skeletons, from other anionic surfactants that have no fluoro-carbon skeletons. We advance the fluoro-SPE protocol to enable the extraction of fluorosurfactants using 4-5 times (in volume) more solvent for fluorophilic eluting in effort to overcome the strong interaction between the fluorosurfactants and the fluoro-Gel. Based on a smartphone-based app we developed recently to assess the colouration of fluorosurfactants with a dye (ethyl violet) that is similar to MBAS (methylene blue active substances), plus an SPE for pre-concentration and fluoro-SPE for pre-selection, we successfully achieve a detection limit of 1 ppb for the PFAS including perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and 6:2 fluorotelomer sulfonate (6:2FTS), which is encouraging and can be conducted in a general laboratory.

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) constitute a family of organic compounds. Their fluoro-carbon skeletons exhibit different properties from others of hydrate-carbon, chloride-carbon origin, etc. PFASs have the unique property of simultaneous hydrophobicity and oleophobicity that, according to the evidence, does not exist in other compounds (Buck et al., 2011; Prevedouros et al., 2006). Consequently, PFASs have been used in many applications in industry, ranging from anti-stunting painting, to carpeting and clothing industries, to fire-fighting foam, etc. (Moody and Field, 2000; Prevedouros et al., 2006; Wang et al., 2014a,b,c) Unfortunately, the fluoro-carbon bond is one of the most stable covalent bonds in existence and resistant to thermal/chemical degradation (Fang et al., 2017b). Their widespread applications and inertness have led to their global distribution (Wang et al., 2014a,c) and the subsequent danger they pose to human and animal lives, and bio-accumulation in the natural environment (Taniyasu et al., 2003). Two good examples are perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), both of which are fluorosurfactants (FSs) and the latter has been previously formulated in aqueous film-forming foams (AFFFs) (and other industrial applications as well). Recently, they have been listed as emerging contaminants and persistent organic pollutants (EPA, 2014).

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Obviously, monitoring of PFOA and PFOS in the environment is urgently needed (Place and Field, 2012; Shoemaker et al., 2009). Currently, their detection is carried out in professional laboratories using HPLC and capillary electrophoresis, which is usually expensive and not available in general laboratories (Fang et al., 2015, 2018). It is thus desirable to develop a pre-screening tool to enable a specific test in a general laboratory. Recently, we have tried Surface-enhanced Raman scattering (SERS) (Fang et al., 2016), Molecularly Imprinted Polymer (MIP) technique (Fang et al., 2017a), along with others to identify this issue (Gong et al., 2015). However, only limited success has been achieved so far. The possible reason for this is that the concentration of fluorosurfactants is usually extremely low, such as at ppb (part per billion) level (Taniyasu et al., 2003), which is much lower than the common inorganic ions in surface water or ground water (such as at ppm, part per million, level) (Thunqvist, 2004). How to extract FSs to remove the background interference and to pre-concentrate FSs is a challenge. Usually, this challenge is overcome using solid-phase extract (SPE) or liquid-phase extraction (LPE). Whilst SPE/LPE can extract FSs when removing the background inorganic ions to benefit the subsequent test, (Tang et al., 2015) they can extract other anionic surfactants (ASs) as well, such as sodium dodecylbenzenesulfonate (SDBS), a commonly used detergent, which means the interference is still occurring.

Fortunately, fluoro-SPE has been well established recently to separate fluoro-tagged compounds from the rest (Matsugi and Curran, 2004; Zhang and Curran, 2006). The selective separation is based on the unique interaction between the tagged fluoro-carbon groups and the fluoro-Gel. Due to unique fluoro-chemistry and the strong interaction among the fluoro-carbon groups, the tagged fluoro-carbon skeletons can suffer fluorophobic washing and remain on the fluoro-Gel, whilst other compounds that contain no fluoro-carbon skeleton are washed off during this fluorophobic washing process. Consequently, fluoro-carbon tagged compounds can be selectively extracted and separated from the remaining anionic surfactants (Xiong et al., 2013; Xu et al., 2015).

Because FSs also yield fluoro-carbon skeletons, fluoro-SPE has been reported in studies analysing PFOA, PFOS and others (Xu et al., 2015). However, the selective extraction of FSs from other surfactants has not been demonstrated (Deng et al., 2014). FSs exhibit differences from the fluoro-tagged compounds because FSs only contain the straight fluoro-carbon skeletons (in some cases, a branched isomer is co-existent). Those straight fluoro-carbon chains might display a strong interaction with the fluoro-Gel and cause difficulty in fluorophilic elution.

To confirm the above hypothesis, we employ fluoro-SPE to separate FSs from other interferences after the SPE pre-concentration process. In this case, SPE can concentrate FSs to benefit the detection sensitivity whilst the fluoro-SPE will benefit the selectivity by removing the possible inference arising from the non-fluoro-surfactants. By combining those two processes which can be carried out in a typical laboratory, we can successfully detect FSs down to 1 ppb. Furthermore, a smartphone-based app can read the colouration of the test reaction (Fang et al., 2018), enabling this to serve successfully as a pre-screening tool with a high level of sensitivity and selectivity.

2. Materials and methods

2.1. Chemicals and materials

All chemicals including PFOA, PFOS, 6:2 fluorotelomer sulfonate (6:2FTS), SDBS, styrene-divinylbenzene polymer resin (SDVB), fluoro-Gel, acetone, methanol, ethyl acetate and ammonium acetate (NH_4Ac) were purchased from Sigma-Aldrich (Australia). AstkCARE^{TM} reagent (ethyl acetate: acetone: ethyl violet, 3: 3: 1 in volume) was provided by CRC CARE (Australia). Only polypropylene containers/pipette tips were used throughout (Fang et al., 2015). Milli-Q water (MQ water, > 18 M$\Omega\bullet$cm) was used in the present study. Furthermore all the standard samples were diluted in MQ water in centrifuge tubes (polypropylene) without pre-treatment unless indicated. All the experiments were carried out at room temperature ($\sim$24 $^\circ$ C).

2.2. Sample preparation: SDVB-SPE and fluoro-SPE

To expand the application, PFOA/PFOS / 6:2FTS was spiked in tap water for tests. In this case, tap water was collected at Callaghan campus, University of Newcastle, NSW, Australia. For better performance, tap water (spiked with PFOA/PFOS / 6:2FTS) was boiled for 1–2 min and then cooled down to the room temperature for further testing.

SDVB-SPE was carried out using 0.1 g SDVB as the absorbing matrix with the help of a vacuum, as recommended by USEPA (EPA/600/R-08/092)(Shoemaker et al., 2009). Basically, a 500 mL aqueous sample (spiked tap water) flowed through the cartridge containing the SDVB powder resin. The resin was then washed with 5 mL MQ water 5 times to remove the potential interfering moieties. After washing, the absorbed ASs were eluted with 1 mL methanol. The methanol extract was then concentrated to dryness with nitrogen in a heated water bath. It was then dissolved into 5 mL MQ water for the visual/app test, or to 1 mL MQ water for the subsequent fluoro-SPE.

Fluoro-SPE was conducted as recommended elsewhere (Matsugi and Curran, 2004; Zhang and Curran, 2006), with a little modification. General protocol is to use 0.2 g fluoro-Gel as a filter to remove non-fluoro-carbon compounds. Then the fluoro-Gel was (Step (1)) pre-conditioned with 1 mL 80% methanol solution (20% water, v/v). After that, SDVB-SPE extract of 1 mL was (Step (2)) loaded onto the fluoro-Gel with a vacuum. The cartridge was (Step (3)) washed off with 0.5 mL 80% methanol again to remove other ASs whilst retaining the PFOA/PFOS / 6:2FTS. In the end, the PFOA/PFOS / 6:2FTS was (Step (4)) eluted with 20 mL methanol. Similarly, the methanol extract was concentrated to dryness and then dissolved into 5 mL MQ water for the app/visual test with 3.5 mL of astkCARE^{TM} testing reagent (Fang et al., 2015).

2.3. Sample analysis

Samples were analysed using an astkCARE^{TM} testing kit (CRC CARE, Australia) for the visual/app test (George and White, 1999; Megharaj et al., 2011) and HPLC-MS (Agilent 1260 + Quadrupole 6130) for validation (Boulanger et al., 2004; Taniyasu et al., 2003). The astkCARE^{TM} testing kit needs a 10 mL aqueous sample to be mixed with 7 mL astkCARE^{TM} reagent. After shaking for ∼10 s and then keeping it static for 1–2 min, the organic phase's top layer extracted the ion-pair of the cationic dye and the ASs, including FSs. Similar to the MBAS (George and White, 1999), the brightness of the organic phase corresponds with the ion-pair concentration and thus provides a test of AS concentration with a limit of detection of 0.1 ppm for the visual test (Fang et al., 2015), or 10 ppb for the smartphone app test, as reported recently (Fang et al., 2018). However, we reduced the amount herein to one half. That is, a 5 mL sample was mixed with 3.5 mL astkCARE^{TM} reagent in an effort to save the sample. Consequently, a flat-bottom tube with an inner diameter of 1.4 cm, rather than 2.5 cm, was used as an extraction container to get an obvious organic phase of top layer for the colour justification. The shortened absorption length, from 2.5 cm to 1.4 cm, means the standard deviation is accordingly increased, from ∼10% to ∼20%, for the smartphone app test (Fang et al., 2018).

For HPLC-MS analysis, we followed the standard method (EPA/600/R-08/092) (Park et al., 2009). In general, a 10 μL sample solution was injected into Agilent 1260 high-performance liquid chromatography fitted with an Eclipse plus-C18 column kept at 40 ° C with the following dimensions: 4.6 mm internal diameter, 100 mm length and 3.5 μm particle size. The flow rate was 0.5 mL/min for the gradient mobile phase of methanol: 5 mM aqueous NH_4Ac for separation. The quadrupole 6130 detector was maintained under negative mode for scanning. Extraction of the molecular ions was conducted at m/z 413 for PFOA, 499 for PFOS, respectively. Quantification was carried out by producing a calibration curve using standard solutions of PFOA, PFOS (only linear isomers) with correlation coefficients higher than 0.99 and limit of detection ∼0.2 ppb (signal : noise > 3). Blank samples of HPLC-grade MQ water and methanol were run prior to each test set to minimize the background contamination that might originate from the Teflon components of the HPLC instrument itself. The nebulizer gas (nitrogen) pressure was set at 35 psi, drying gas flow rate was 10 L/min and temperature 350 °C, the capillary voltage was + 3500 V(Vecitis et al., 2008).

Note that each time we ran at least 3 samples in parallel (2 standard samples for calibration whilst 1 sample for test) for quality assurance and quality control (QA/QC) (Wang et al., 2014a).

3. Results and discussions

3.1. Fluoro-SPE procedure.

Fig. 1 shows the Schematic drawing of the SPE including SDVB-SPE and fluoro-SPE. As stated, we employed SDVB to pre-concentrate FSs, which are described in another report (Fang et al., 2018). Consequently, the concentration could be increased by 10–200 times, which depends on the volume of the sample before and after the SPE. In this report, we concentrate the FS sample from 500 mL to 5 mL (100 times of the concentration increase) and focus on fluoro-SPE to target FSs.

We initially tried to combine SDVB-SPE with fluoro-SPE together by simultaneously packing them into a column (0.1 g SDVB on the top and 0.2 g fluoro-Gel on the bottom), which yields a slow extraction process due to the slow flow speed (> 3.5 h for 1 L sample). To overcome this problem, we conducted SDVB-SPE and fluoro-SPE individually to accelerate the process, as shown in Fig. 1. The period has been shortened to ∼1.5 h (∼1 h for SDVB-SPE and ∼0.5 h for fluoro-SPE).

As stated in Fig. 1 (bottom), there are 4 steps for fluoro-SPE: pre-conditioning (1), sample-loading (2), fluorophobic washing (3), and fluorophilic eluting (4). Whilst the pre-conditioning using 1 mL 80% methanol is normal, we focus our research on Steps (2–4) using spiked MQ water samples and then expand to the spiked tap water samples.

3.2. Effect of sample loading at step (2).

We selected the fluoro-Gel of 0.2 g for extraction because the recommended maximum loading amount is in the 10–30 mg range (Matsugi and Curran, 2004; Zhang and Curran, 2006). This means 2000–6000 ppm FSs if dissolved into 5 mL MQ water that we need for testing in this report, and is much higher than the FSs level of ppb. Decreasing the amount of fluoro-Gel makes the operation difficult, and leads to the appearance of leakage and breakthrough. Conversely, increasing the fluoro-Gel will lead to the elution problem in Step (4), as discussed in more detail below.

In Fig. 2, we loaded 0.5 mL 10 ppm PFOA in MQ water. This amount of PFOA was selected because it corresponded with 500 mL of the sample containing 10 ppb of PFOA for SDVB-SPE, which is the targeted volume and concentration range (upper limit, also the detection limit of the smartphone app) in this report. From the middle column, we see the colour is almost the same as the control samples of MQ water (right column), whether for PFOA or SDBS, suggesting both of them have been loaded onto the fluoro-Gel. The blue column on the left confirms the loading because the loaded PFOA and SDBS were successfully eluted for the visual test.

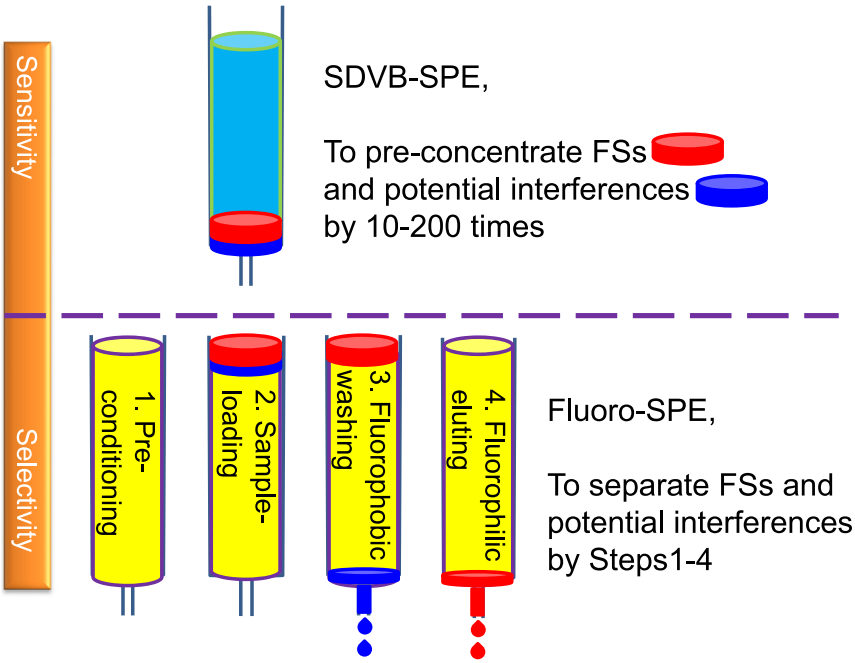

Fig. 1. Schematic drawing of the Fluoro-SPE after SDVB-SPE.

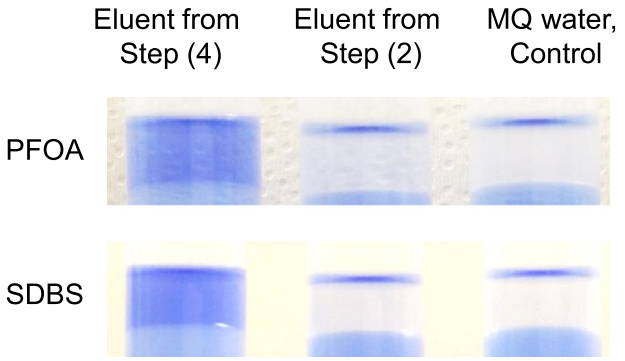

Fig. 2. Visual tests subjected to Step (2) using astkCARE^{TM}. The general protocol was followed except in Step (2), where 0.5 mL 10 ppm PFOA or SDBS was loaded and Step (3) has been bypassed.

3.3. Effect of fluorophobic washing at step (3).

Before fluorophilic eluting, the fluorophobic washing process is designed to remove possible interference (such as SDBS) while retaining the FSs, which is critical for the selectivity of the test. Therefore we need to optimize the fluorophobicity of the washing solvent and its amount.

In Fig. 3, the effect of fluorophobic washing was tested. When the concentration of methanol was higher than 50%, SDBS was gradually washed off whilst only a limited amount of PFOA was washed off (eluent from Step (3)). Evidence for this is provided by the smartphone app test (top) and visual test (bottom). The remaining PFOA and SDBS on the fluoro-Gel were also detected and confirmed the above observation (eluent from Step (4)). Therefore we fixed the fluorophobic washing solvent consisting of 80% methanol (20% water) at Step (3) for the following tests. A higher concentration of methanol may lead to a significant washing-off of the PFOA at this step, so for this reason it was not selected.

The amount of fluorophobic washing solution was 0.5 mL. However, given the result shown in Fig. 4, a little more washing solution did not lead to a significant change in the result.

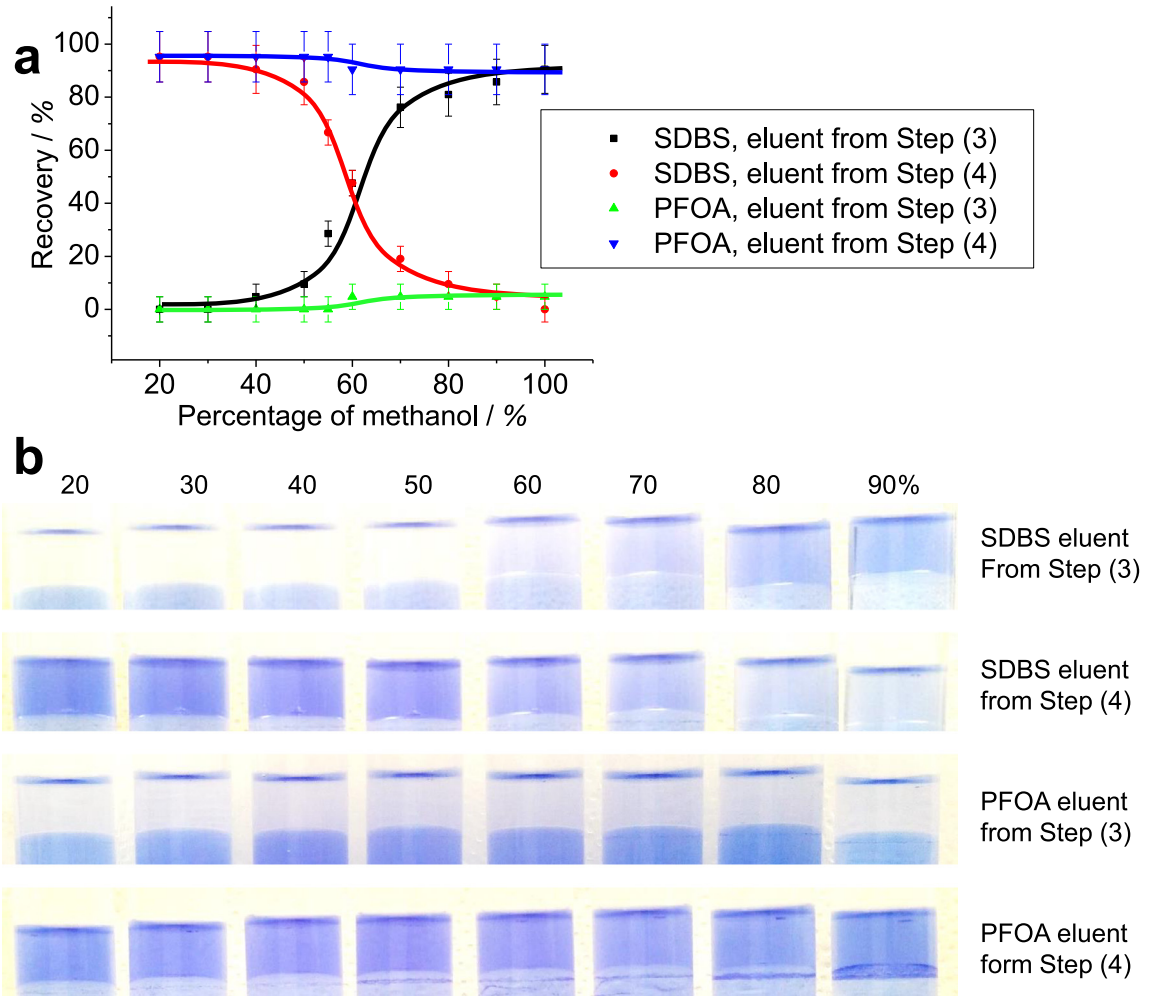

Fig. 3. App (top) and visual tests (bottom) subjected to the fluorophobic washing solvent in Step (3). The general protocol was followed as shown in Fig. 2, except in Step (3), where the washing solvent was collected and dried. It was then dissolved into 5 mL MQ water for astkCARE^{TM} visual/app test and presented as "eluent from Step (3)". The fluoro-Gel was then subjected to Step (4). After drying, it was then dissolved into 5 mL MQ water as per the app test and presented as "eluent from Step (4)". The top figure shows the depending curve using the smartphone app whilst the bottom depicts the photo images. The percentage of methanol/water (v/v) in the washing solvent was suggested.

3.4. Effect of fluorophilic eluting at step (4).

Fig. 4 shows the testing results following Step (4). No fluorophobic washing was done in order to avoid any possible loss of PFOA. We can see that the elution of PFOA appeared at 5 ml onwards, until 25 mL, whether the eluting solvent was methanol or acetone (both at 100%). Consequently, we used 20 mL methanol as the eluting solvent in order to completely elute FSs in further tests.

It should be noted that this is much higher than the recommended methanol amount (20 mL *vs.* 4 mL) (Matsugi and Curran, 2004; Zhang and Curran, 2006). The possible explanation for this is due to the straight fluoro-carbon chain of FSs being different from the fluoro-tagged compounds. In the former case, a FS exhibits a much smaller hydrophilic head of –COOH or -SO_3H than the fluoro-carbon chain. In the latter case, a tagged compound usually has a bigger moiety than the fluoro-carbon chain. The fluoro-carbon skeletons whether from FSs or from tagged compounds might be inserted into the fluoro-carbon monolayer on the fluoro-Gel surface (-$SiMe_2$ $(CH_2)_2C_8F_{17}$) (Fang et al., 2017c). The small hydrophilic groups of FSs could experience elution difficulty when compared to the tagged big moiety. In the latter case, the compounds' main structure floats on the surface of the monolayer of -$SiMe_2$ $(CH_2)_2C_8F_{17}$. Only the fluoro-tag interacts with the fluoro-matrix. Consequently, the fluoro-tagged compounds are easier to be fluorophilic-eluted than the FSs tested here.

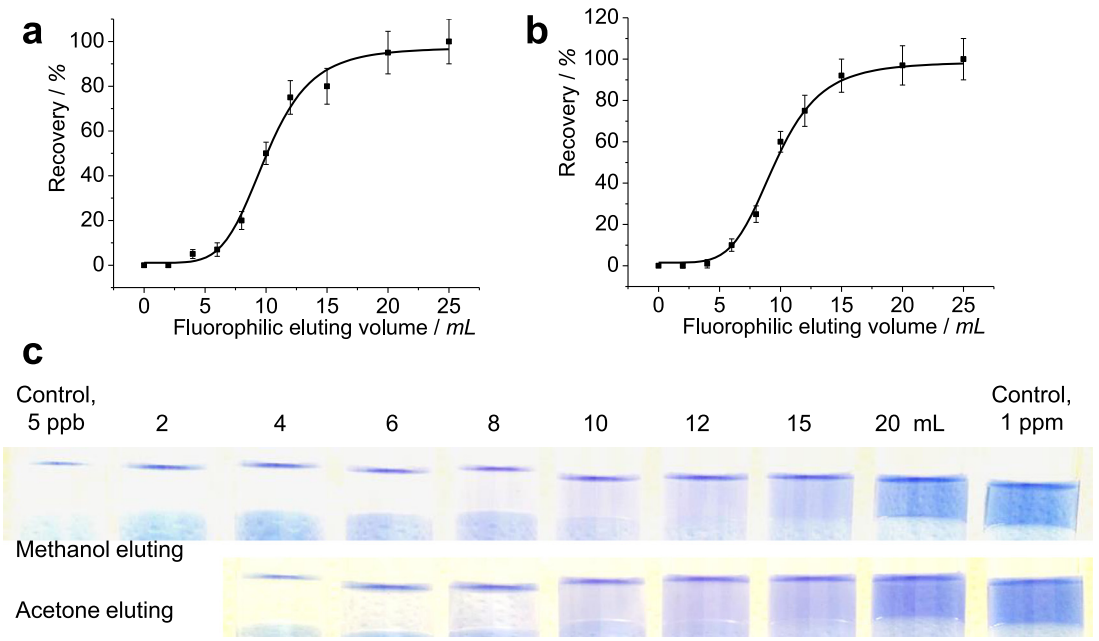

Fig. 4. App (top) and visual tests (bottom) subjected to the fluorophilic eluting amount in Step (4). The general protocol was followed except that no fluorophobic washing occurred in Step (3). (a) and (b) were subjected to methanol and acetone washing, respectively.

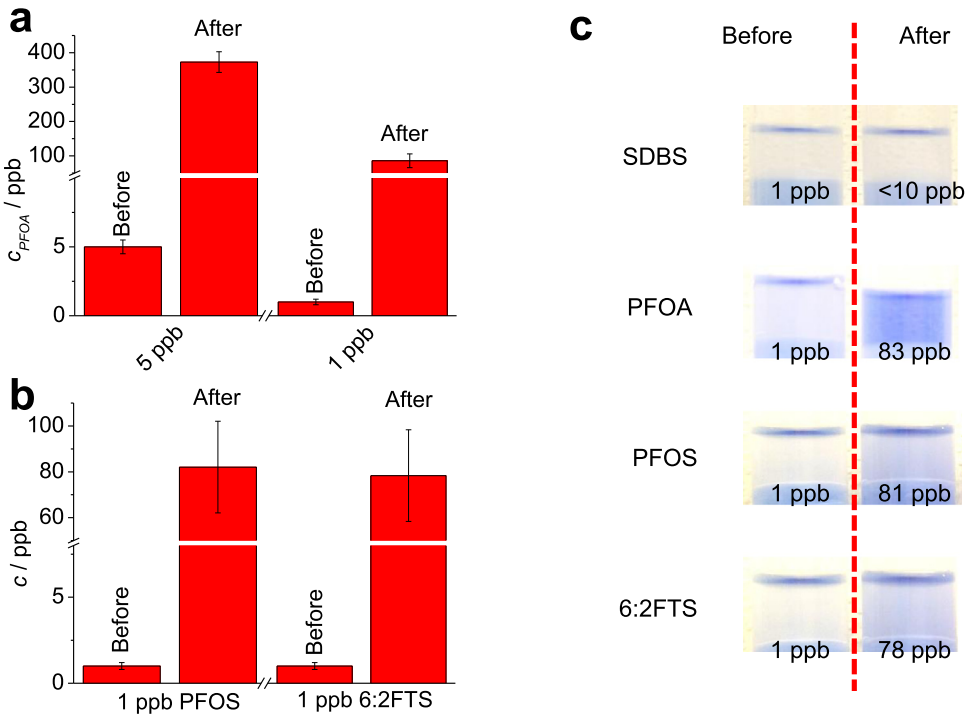

Fig. 5. HPLC-MS results (a, b) and visual/app test (c) of SPE including SDVB-SPE and subsequent fluoro-SPE when fluorosurfactants were spiked in tap water. (a) shows the results for the PFOA test whilst (b) for the PFOS/6:2FTS test, as indicated. In (c), the concentrations before (left, spiked in MQ as control) and after the treatment (right, app testing results) are indicated. The general protocols of SDVB-SPE and fluoro-SPE were followed as highlighted in the text.

3.5. Combined fluoro-SPE with SDVB-SPE

After combined the fluoro-SPE (to benefit selectivity of the fluorosurfactant detection) with the SDVB-SPE (to benefit sensitivity of the fluorosurfactant detection), we validates this approach utilizing HPLC-MS. In Fig. 5(a) we can see that PFOA has been successfully extracted after SDVB-SPE and the subsequent fluoro-SPE with a recovery rate of ∼73% from tap water. The variation of the recovery rate is relatively large, from 60% to 85%, which is due to the two SPE procedures, in which some PFOA was lost and not completely recovered. Furthermore, Fig. 5(b) illustrates the testing results concerning two more FSs, PFOS and 6:2 FTS, which are often monitored for environmental protection. Again, we can see that the limit of detection of 1 ppb was successfully achieved, as evidenced by the visual/app test in Fig. 5(c). In the meantime, SDBS features almost no interference, suggesting this approach succeeded in sensitively and selectively detecting FSs. In fact, this level can be pushed down to 0.5 ppb when a more sensitive app test is employed, even for ground water, as reported elsewhere (Fang et al., 2018).

4. Conclusion

In general, FSs have been successfully extracted and detected using visual and app tests. The extraction using the astkCARE^{TM} reagent acts to form an anionic surfactan-t-cationic dye ion-pair, which is similar to methyl blue active substances (MBAS). This ion-pair is immiscible in aqueous solution and therefore can be extracted to the organic phase for colour justification, if not using a spectrometer. Based on the colour, a visual assessment or smartphone-based app can relate it to the concentration level. In order to improve the sensitivity, SDVB-SPE was employed to concentrate the sample from 500 mL to 5 mL, whilst fluoro-SPE was employed to selectively extract FSs from ASs. Since a limit of detection of 1 ppb was achieved for PFOA, PFOS and 6:2FTS, it has been shown that the approach is successful. It confirms that FSs testing can be undertaken in typical laboratories where extraction is available. The validation of this protocol for the detection of other FSs, including different length of carbon chains and different functional groups, is ongoing in our laboratory.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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