Determination of Perfluorooctanoate and Perfluorooctanesulfonate in Water Matrices by Inline Matrix Elimination Liquid Chromatography with Reversed Phase Separation and Suppressed Conductivity Detection

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Abstract

This work describes a new method for the determination of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) in water matrices by suppressed conductivity detection. Separation was achieved by isocratic elution on a reversed-phase column thermostated at 45°C using an aqueous mobile phase containing boric acid and acetonitrile. The PFOA and PFOS content in the water matrix were quantified by a pre-concentration technique. For the concentration range of 1 to 15 ng/mL and 2 to 30 ng/mL, the linear calibration curve for PFOA and PFOS yielded coefficients of determination (R^2) of 0.9995 and 0.9985, respectively. The relative standard deviations were smaller than 1.5% for PFOA and PFOS. The retention-time precision of four consecutive 12 h injections was smaller than 0.641% and 0.818%, respectively. The presence of common divalent cations, such as calcium, magnesium, and iron in water matrices impairs PFOS recovery. This drawback was overcome by applying inline matrix elimination method. The optimized method was successfully applied for drinking water, ground water, and seawater samples.

Introduction

Perfluorinated compounds (PFCs) have been widely used in industrial and consumer applications including stain- and water-resistant coatings for fabrics and carpets, and oil-resistant coatings for paper products approved for food contact, fire-fighting foams, mining and oil well surfactants, floor polishes, and insecticide formulations. Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the two typical perfluorochemicals representing this group of chemicals, and they are frequently found in different environmental matrices, from ocean water to a variety of foodstuff. Until now, several studies have been reported on the analysis of PFCs at a very low concentration level in water samples (1–18), soil (19,20), wildlife tissues (21–23), human whole blood (24), fish (2,25), serum and plasma (26–29), and other biological samples.

The detection of these compounds in surface water, groundwater, and drinking water raises considerable public concern. Especially when human health-based guideline values are not available it raises concern if the detected concentration levels are harmful to affect human health. PFOA and PFOS are environmentally persistent compounds and their increasing occurrence in drinking water and its sources should be monitored closely. Surface water and wastewater collected from several countries have been shown to contain PFCs. Many of them combine bioaccumulative potential toxic effects and extreme persistence, thus they are considered as candidates for priority organic pollutants under the Stockholm Convention for global regulation on production and use, and regarded as a new and emerging class of environmental contaminants (30). They have been proposed as new priority substances of the Water Framework Directive (WFD) by the European Parliament. The state of the art in monitoring chemical pollutants to assess water quality status according to WFD and the challenges associated with it have been reviewed (31).

The rapidly-expanding research on commercially important perfluorinated alkyl substances, such as PFOS and PFOA, has resulted in a wide range of analytical methods to determine their human and environmental exposure potential. So far, most of the analytical methods to determine PFCs are based on liquid chromatography coupled to mass spectrometry or tandem mass spectrometry (LC–MS or LC–MS–MS) (32). Matrix effects (i.e., ionization suppression or enhancement) in PFC quantification using electrospray mass spectrometry LC–MS–MS have been a major problem. Several sample preparation methods were applied to overcome the matrix influence. Solid-phase extraction (SPE) is the method of choice for extracting PFCs from water. Liquid–liquid extraction (LLE) is also a suitable sample preparation technique. A wide variety of SPE methods have been reported for sample extraction and cleanup of water samples (33). In order to determine these contaminants at trace level in environment samples, pre-concentration is usually necessary.

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In this paper we report a novel method of analyses using suppressed conductivity detection and optimization of chromatographic conditions and technique for cleanup of different water matrices.

Materials and Methods

Instrument

For all experiments a professional ion chromatograph with a built-in sample preparation module, model number 850, from Metrohm (Herisau, Switzerland) was used. The instrument control and data collection were carried out with MagICNet software. A Prontosil 120-5-C18-ace-EPS column containing 5 µm particles (4.0 mm × 150 mm) from Bischoff, Germany was used for separation, and its guard column was used for sample preconcentration. It had a working pH range from 2 to 10. The 827 pH meter with the Aquatrode-Plus electrode from Metrohm was used for the mobile phase pH adjustment and the buffer preparations.

Chemicals and reagents

All solutions were prepared using deionized water (> 18 MΩ) purified by a Milli-Q Gradient system (Millipore, Billerica, MA). PFOA (96%, Aldrich, Cat. No.: 171468), PFOS (98%, Fluka, 33827), boric acid, (Biochemica grade, Fluka, St. Louis, MO 15662), sodium bicarbonate (Puriss grade, Fluka, 31437, sodium hydroxide (50% for IC, Fluka, 72064) and sodium chloride, (Biochemica grade, Fluka, 71378) were bought from Sigma-Aldrich, Bangalore, India. Sulphuric acid (Suprapure Merck, Darmstadt, Germany, 1.00714) and acetonitrile (HPLC grade, Merck India, 600030) were bought from Merck, Darmstadt, Germany.

Mobile phase and regenerent solutions

A mobile phase solution containing 20 mmol/L boric acid and 38% acetonitrile was prepared by weighing accurately 2.48 g of boric acid and transferring it to a 2.0 L eluent container, so that 1240 mL of ultrapure water was added and sonicated until it dissolved. Then the pH of the solution was adjusted to 8.0 with 4.0 mol/L sodium hydroxide. 760 mL of acetonitrile was added to the solution and ultra sonicated for 10 min. The prepared mobile phase was filtered through a 0.2 µm nylon filter under vacuum.

100 mmol/L sulfuric acid and ultrapure water were used as the regenerent and rinsing solution for the suppressor. For the inline sample preparation, respectively, 50 mmol/L sulfuric acid and 100 mmol/L sodium chloride were used as the regenerent and rinsing solutions.

Borate buffer

First, 1.24 g of boric acid was accurately weighed into a 100-mL beaker and dissolved with 95 mL of water. Then the pH was adjusted to 8.0 with 4 mol/L sodium hydroxide and finally made up to the total volume of 100 mL.

Standard solution

Exactly 0.1042 g of perfluorooctanaic acid was weighed and transferred completely into a 100-mL volumetric flask. The substance was dissolved in ultrapure water and made up to the mark with water to obtain a concentration of 1000 µg/mL of PFOA.

Exactly 0.1020 g of perfluorooctanesulphonic acid was weighed and transferred completely into a 100-mL volumetric flask and dissolved in ultrapure water and made up to the mark with water to obtain a concentration of 1000 µg/mL of PFOS. For lower concentrations of PFOA and PFOS preparation, a 0.1 mL of buffer was added per 10 mL of standard solution.

Results and Discussion

Chromatographic optimization

Influence of buffer concentration

The separation of PFOA and PFOS was tried using the reverse phase column with borate and bicarbonate buffers. The influence of the buffer concentration was studied by increasing aqueous buffer concentration while the buffer pH and acetonitrile concentrations remained constant. The influence of buffer concentration on PFOA and PFOS separation is shown in Figure 1A and 1B; as the borate concentration increased, the retention factor for both the components increased, indicating a stronger binding with the stationary phase due to ion pair formation. An increase of five to ten-fold in the retention factor value was noticed when the borate buffer concentration was increased

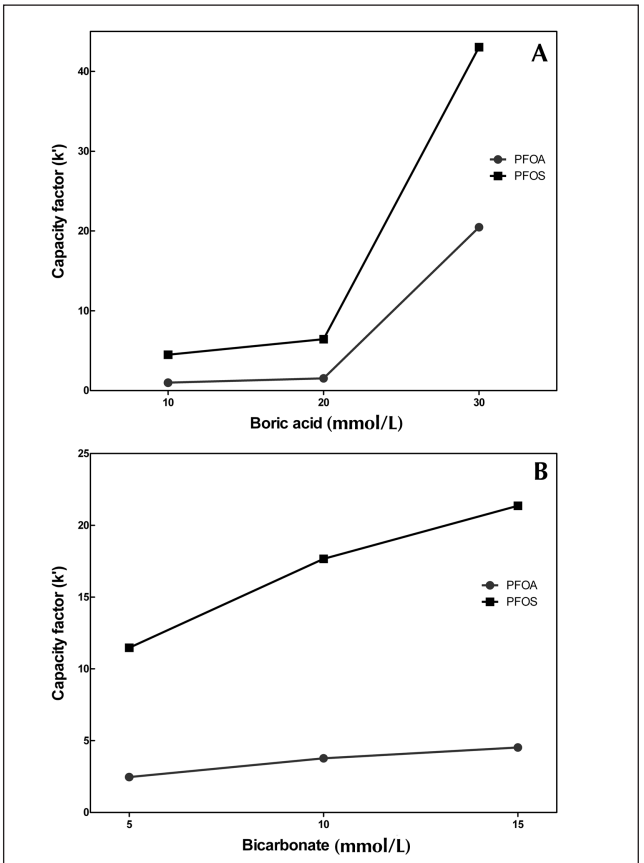

Figure 1. Influence of the buffer concentration on PFOA and PFOS separation. (A) borate buffer; (B) bicarbonate buffer.

from 20 mmol/L to 30 mmol/L. The retention factor also increased with the increase of the bicarbonate buffer, but the was not as significant as that of the borate buffer. For all further studies, 20 mmol/L of the borate buffer was used.

Influence of organic modifier

The influence of an organic modifier was studied by varying the concentration of methanol and acetonitrile while the aqueous buffer concentration and pH were kept constant. The increase in the organic modifier concentration resulted in the reduction of the retention factor for both components. At least 50% of the methanol in the mobile phase was necessary to elute both components, while they were eluted with the mobile phase containing just 25% of acetonitrile. Hence, for the subsequent characterization, acetonitrile was used. The retention behavior is shown in Figure 2A and 2B.

The increase in the aqueous buffer concentration led to retention, while the organic modifier reduced retention. It is an ideal condition to run a binary gradient from lower acetonitrile concentration to higher to get a good separation of PFCs. However, to make the system configuration simple and economical, an isocratic separation condition is optimized.

Influence of column oven temperature

The column oven temperature was varied from 35°C to 50°C. The increase in temperature resulted in an inverse behavior for PFOA and PFOS. With the increase in column oven temperature, a significant reduction in the retention factor was observed for the late-eluting PFOS component, whereas an increase in the retention factor was noticed for PFOA. The temperature influence is shown in Figure 3. The optimal temperature of 45°C was selected for further work.

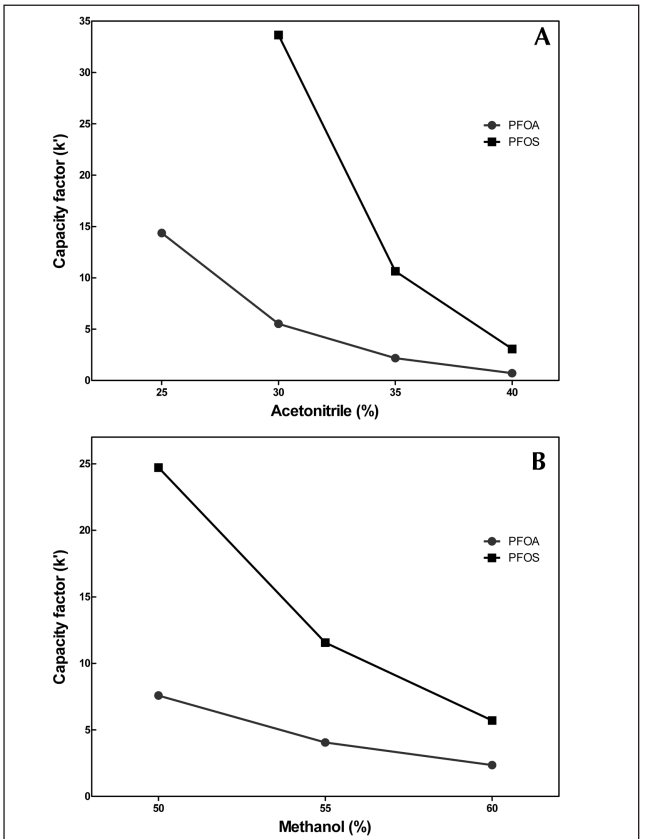

Figure 2. Influence of organic modifier on PFOA, PFOS Separation. (A) eluent with acetonitrile; (B) eluent with methanol.

Influence of eluent pH

The 827 pH meter with the Aquatrode Plus electrode was calibrated using buffers 7.00 and 9.2. The aqueous buffer pH was adjusted using 4 mol/L sodium hydroxide. The influence of the aqueous buffer's pH on the retention factor was studied from 7.4 to 8.8. As the pH increased, the retention factor for both the components increased. The influence of the pH is shown in Figure 4.

Sample pre-concentration

To improve the detection limit, the guard column was used as the pre-concentrator column. A 2.5-mL sample loop was connected to the six port injection valve of the 858 sample processor. Standards and samples were filled to the loop using the peri-

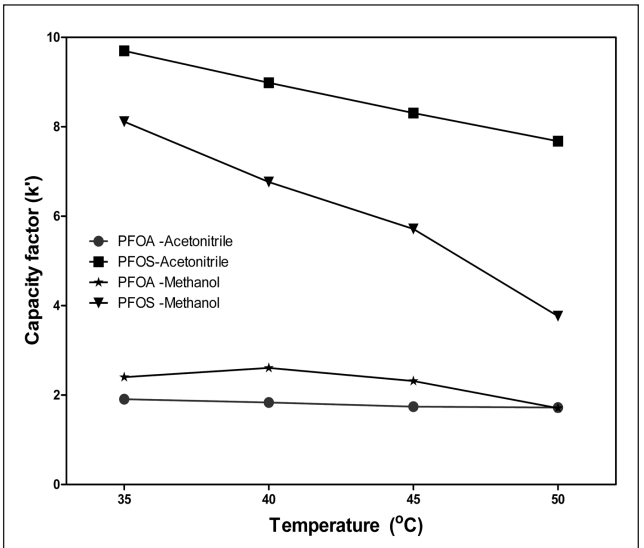

Figure 3. Influence of column oven temperature on PFOA and PFOS separation.

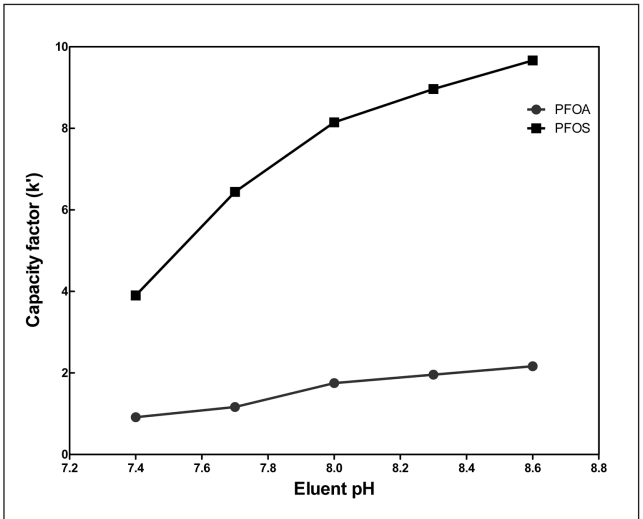

Figure 4. Influence of eluent pH on PFOA and PFOS separation.

staltic pump built-in on to the 858 sample processor. Loaded samples and standards were pre-concentrated onto the guard column, installed on the IC injector by a high pressure pump. The pre-concentration volume was varied from 5 mL to 20 mL. Pre-concentration volumes higher than 10 mL resulted in an analyte loss, and hence the pre-concentration volume was fixed at 10 mL. The optimized chromatography condition involved a 20 mmol/L boric acid buffer pH adjusted to 8.0 and 38% acetonitrile. The column oven was set at 45°C. The eluent flow rate was set to 1.0 mL/min and the suppressed conductivity detection was used. The sample pre-concentration volume was 10 mL. The chromatogram obtained under the optimized chromatographic condition is shown in Figure 5.

System precision

To check the system precision, a mixed standard containing 2 ng/mL PFOA and 10 ng/mL PFOS was injected six times. The resulting relative standard deviation (RSD) percent was calculated for PFOA and PFOS as 1.15% and 1.06%, respectively.

System and standard solution stability

Short-term stability of the chromatographic system was tested for 36 h. A mixed standard containing 5 ng/mL PFOA and 10 ng/mL PFOS was prepared and kept in a polypropylene (PP) vial in a sample processor at room temperature, and was injected every 12 h to 36 h. From the retention time and area of the standard, the stability of the chromatographic system as well as the stability of the standard and the sample in the PP vial was evaluated.

The retention time for PFOA varied from 4.26 min to 4.31 min with an RSD of less than 0.641%. For PFOS, the retention time (RT) varied from 18.19 min to 17.88 min with an RSD of less than 0.818%. This study proved that the short-term stability of the chromatographic system is good and it is suitable for continuous quantification of PFOA and PFOS. The concentration of the PFOA standard varied from 5.00 ng/mL to 4.804 ng/mL with an RSD of 1.86%. The concentration variation for the PFOS standard was from 10.00 ng/mL to 9.803 ng/mL with an RSD of 1.84%. This study indicates that the buffered standards are stable up to 24 h in the PP sample vial at room temperature. The RT and the concentration stability are shown in Figure 6.

The buffer addition ensured the complete ionization of PFOA and PFOS and eliminated their adsorption on the surface of the sample vials.

Linearity

A standard solution of mixed PFOA and PFOS concentration ranging from 1.0 ng/mL to 15 ng/mL, and 2.0 ng/mL to 30 ng/mL, respectively, were prepared by an appropriate dilution of the standard stock solution with buffer and water. Each standard was injected thrice to check the precision at each concentration level.

A regression line was obtained by plotting the peak area (µS/cm × s) for PFOA and PFOS using the least square method. The relationship between the peak response and the concentration was found to be linear between the ranges of 1 ng/mL to 15 ng/mL of PFOA with the correlation coefficient (r^2) of 0.9995 and a response factor RSD of 1.479%. The r^2 and response factor RSD for PFOS were 0.9985 and 2.895%, respectively, and for the PFOS concentration, from 2 ng/mL to 30 ng/mL.

Limits of detection quantification

The limit of detection (LOD) for PFOA and PFOS was calculated from the residual SD (Sy/x) obtained from the linearity data using the formula LOD = (Sy/x × 3.3)/slope and limit of quanitification (LOQ) = (Sy/x × 10)/slope. The Sy/x and the slope for PFOA are 0.0003847 and 0.003424, respectively, and the LOD and LOQ for PFOA, respectively, were 0.370 ng/mL and 1.12 ng/mL. The Sy/x and the slope for PFOS were 0.0006143 and 0.001529, respectively, and the LOD and LOQ for PFOS, respectively, were 0.383 ng/mL and 4.017 ng/mL.

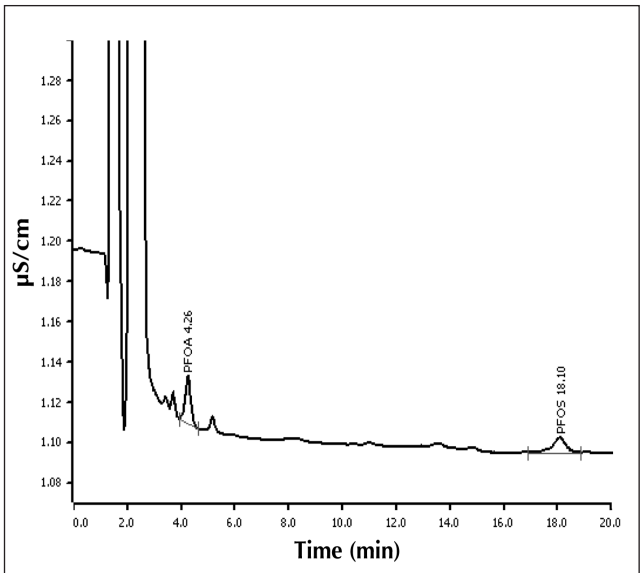

Figure 5. Chromatogram of 1.0 ng/mL PFOA and 2.0 ng/mL PFOS. Column: Prontosil 120-5-C18-ace-EPS column. Eluent: 20 mmol/L borate buffer, pH adjusted to 8.0 and with 38% acetonitrile. Flow rate: 1.0 mL/min. Column oven temperature: 45°C. Pre-concentration volume: 10 mL.

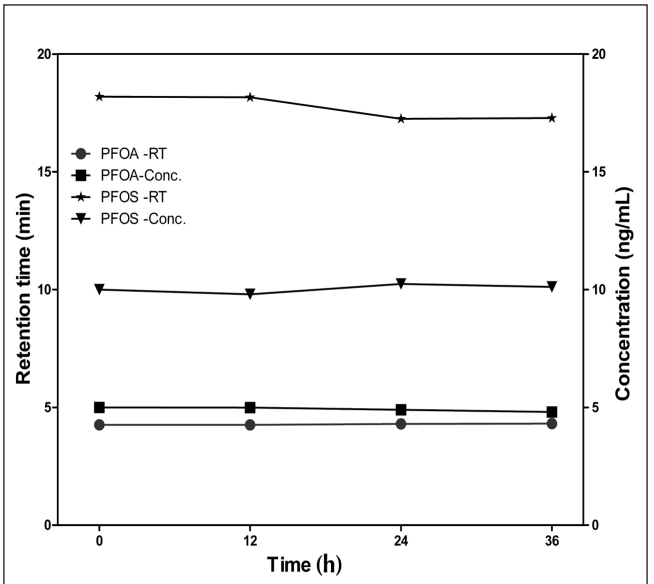

Figure 6. Stability of chromatographic system and standards.

Analysis in Water Matrices

Sample analysis

Using the previously mentioned method, several batches of drinking water from the market were analyzed, and PFOA and PFOS were not detected. The drinking water samples were spiked with 4 ng/mL PFOA and PFOS. PFOS was not detected; however, the RT of PFOA was shifted. This indicated a matrix influence in the drinking water sample. Two groundwater samples and seawater samples were also tested for PFOA and PFOS content. A recovery of less than 20% for PFOA was achieved in these matrices and PFOS was not detected at all, indicating a strong matrix influence.

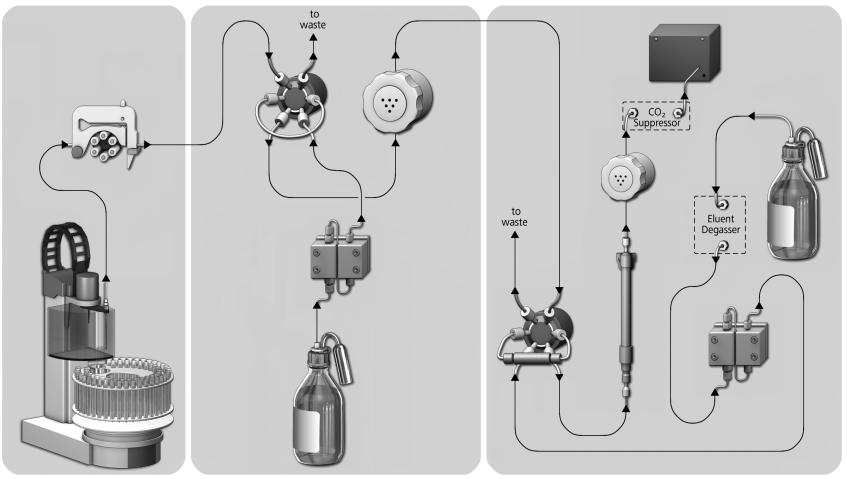

Figure 7. Experimental setup.

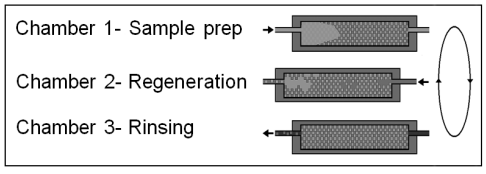

Figure 8. MISP functional description. Chamber 1 is used for matrix removal. Simultaneously, Chamber 2 is regenerated by sulfuric acid, and Chamber 3 is rinsed with water, sodium salt, or lithium salt.

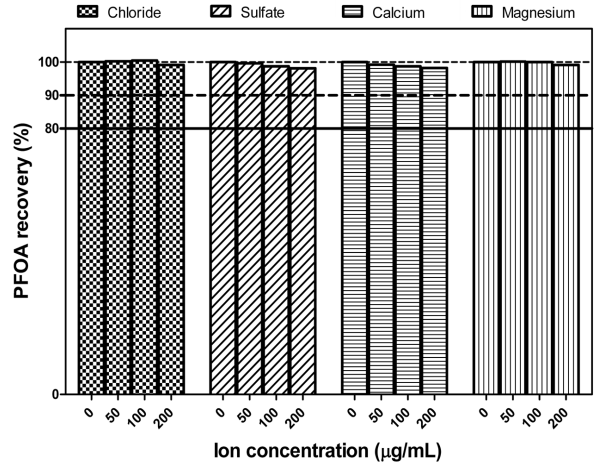

Figure 9. PFOA recovery in the presence of matrix ions.

Matrix influence

The poor recovery in the drinking water sample is a clear indication of a matrix influence. The main ionic components in a drinking water matrix are chloride, sulfate, sodium, calcium, and magnesium. To characterize the matrix influence, mixed standards containing 5 ng/mL PFOA and 10 ng/mL PFOS were spiked with varying concentrations of these matrix ions and the influence of each of these matrix ions on the recovery was studied. Recoveries above 90% for PFOA and PFOS standards spiked with chloride and sulfate matrix ions indicated that their concentration up to 200 µg/mL in the sample had no influence on PFOA and PFOS quantification.

Calcium and magnesium standards prepared from their respective water soluble chloride salts were spiked to the PFOA and PFOS mixed standards, and the recovery was studied. A recovery of less than 70% for standards spiked with 10 µg/mL of calcium and magnesium indicated a clear matrix influence. Divalent cations such as Ca^{2+}, Mg^{2+}, and Fe^{2+} commonly present in water matrices at moderately high concentrations might form complexes with PFO^- and the resultant monovalent complexes (e.g., $PFO–Ca^+$) may elute in the void volume.

This matrix effect study indicates that the direct injection method is suitable for samples containing divalent cations at a concentration less than 10 µg/mL, while for matrices containing higher concentrations of divalent cations, pre-removal is necessary.

Matrix removal

Interfering divalent cations were removed by passing the sample through the Metrohm Inline Sample Preparation (MISP)

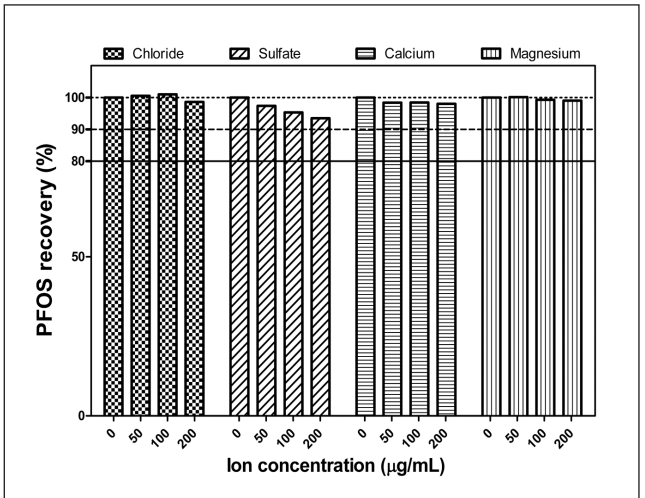

Figure 10. PFOS recovery in the presence of matrix ions.

module, which contains high-capacity packed-bed sulphonic acid resin, wherein the divalent cations were retained and an equivalent amount of hydrogen ions were exchanged. The matrix free sample was filled into the injection loop. The MISP was made up of a trichamber cartridge; one chamber was used for cation removal, the other chamber was regenerated with sulfuric acid, and the third chamber was rinsed with water to remove the sulfuric acid in the line and leave the sulfonic acid resin in the protonated form. Depending on the requirement, either sodium or lithium salts could also be used as a rinsing solution instead of water. An additional peristaltic pump was used for the regeneration and rinsing. The chambers rotated positions as instructed in the software. The instrument setup is shown in Figure 7. The functional description of the MISP is shown in Figure 8.

Table I. Cation Composition of Water Samples

Sample ID	Ion concentration (µg/mL)				
	Sodium	Potassium	Magnesium	Calcium	Iron
Sea water-SW2_5_08	10960	345	1551	576	0.4
Sea water-SW2_4_08	12316	433	1713	503	0.4
Ground water-KB11	74	4.4	14	57	0.07
Ground water-VB15	85.6	5.6	25	42	0.07
Ground water-HB26	62	9	21	77	0.08

Table II. Spike and Recovery

Sample ID	Added (ng/mL)		Found (ng/mL)		Recovery (%)		RSD (%)	
	PFOA	PFOS	PFOA	PFOS	PFOA	FPOS	PFOA	PFOS
Seawater SW2_4_08			4.959	9.687	99.180	96.870		
Seawater SW2_4_08	5	10	4.883	9.507	97.660	95.070	1.23	1.15
Seawater SW2_4_08			5.003	9.488	100.060	94.880		
Seawater SW2_5_08			4.986	9.658	99.720	96.580		
Seawater SW2_5_08	5	10	4.869	9.443	97.380	94.430	1.74	1.35
Seawater SW2_5_08			5.038	9.429	100.760	94.290		
Ground water HB26			4.862	9.879	97.240	98.790		
Ground water HB26	5	10	4.988	9.923	99.760	99.230	1.28	1.08
Ground water HB26			4.917	9.721	98.340	97.210		
Ground water VB15			4.992	9.882	99.840	98.820		
Ground water VB15	5	10	5.162	9.868	103.240	98.680	1.70	1.35
Ground water VB15			5.102	9.647	102.040	96.470		
Ground water KB11			4.926	9.784	98.520	97.840		
Ground water KB11		10	4.898	9.925	97.960	99.250	0.78	1.03
Ground water KB11			4.974	9.982	99.480	99.820		
Drinking water Level 1			1.872	3.803	93.600	95.075		
Drinking water Level 1	2	4	1.804	3.611	90.200	90.275	3.27	2.59
Drinking water Level 1			1.926	3.703	96.300	92.575		
Drinking water Level 2			4.983	10.141	99.660	101.410		
Drinking water Level 2	5	10	5.092	10.189	101.840	101.890	1.61	0.51
Drinking water Level 2			4.931	10.244	98.620	102.440		
Drinking water Level 3			7.905	16.280	98.813	101.750		
Drinking water Level 3	8	16	7.962	16.097	99.525	100.606	0.50	0.80
Drinking water Level 3			8.104	16.204	101.300	101.275		

A recovery of less than 10% was obtained for PFOA; PFOS was not detected when a sample spiked with calcium and magnesium was passed through the protonated sample preparation cartridge by sulfuric acid regenerent and water rinsing, and analyzed. The divalent cations of the free spiked samples were acidic with the pH of approximately 3.0, which caused for the lower recovery.

To adjust the pH of the sample solutions to be close to the eluent pH, the MISP cartridges were saturated with sodium ion by using 100 mmol/L sodium chloride as the rinsing solution. A recovery study was carried out for PFOA and PFOS, spiked with 0 to 200 µg/mL of calcium and magnesium in the sample matrix (drinking water). The recovery values for PFOA spiked with calcium ranged from 98.2% to 100%, and with magnesium ranged from 99.1% to 100%. The recovery values for PFOS spiked with calcium ranged from 98.0% to 100%, and with magnesium ranged from 99.0% to 100%. The achieved recovery was excellent, and the MISP could be used for regular PFOA and PFOS determination in other samples (such as tap water, river water, etc.) containing a high concentration of divalent cations. The recovery details are pictorially given in Figures 9 and 10.

Spike and recovery study

The drinking water samples were spiked with PFOA and PFOS at three different concentration levels. Each spiked sample was injected in triplicate and, from the resulting recoveries, the accuracy and precision of the inline matrix elimination method was evaluated. A recovery from 93% to 101% was obtained for both the species. Ground water and the seawater samples received from the Indian Institute of Science (IISc), Bangalore were characterized for a standard cation and the iron content using IC and voltammetry techniques, respectively. The cation and iron concentration in these water samples are listed in Table I. These samples were spiked with 5 ng/mL of PFOA and 10 ng/mL PFOS and injected in triplicate. A recovery of above 95% was obtained in all the samples. The detailed recovery information together with the cation composition of these samples are provided in Table II.

Acknowledgement

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