Metrohm

Trace-level determination of perfluorinated compounds in water by suppressed ion chromatography with inline matrix elimination

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Summary

This poster describes a simple and sensitive method for the determination of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) in water samples by suppressed conductivity detection. Separation was achieved by isocratic elution on a reversed-phase column thermostated at 35 °C using an aqueous mobile phase containing boric acid and acetonitrile. The PFOA and PFOS content in the water matrix was quantified by direct injection applying a 1000 µL loop. For the concentration range of 2 to 50 µg/mL and 10 to 250 µg/mL, the linear calibration curve for PFOA and PFOS yielded correlation coefficients (R) of 0.99990 and 0.9991, respectively. The relative standard deviations were smaller than 5.8%.

The presence of high concentrations of mono and divalent anions such as chloride and sulfate has no significant influence on the determination of the perfluorinated alkyl substances (PFAS). In contrast, the presence of divalent cations, such as calcium and magnesium, which are normally present in water matrices, impairs PFOS recovery. This drawback was overcome by applying Metrohm`s Inline Cation Removal. While the interfering divalent cations are exchanged for non-interfering sodium cations, PFOA and PFOS are directly transferred to the sample loop. After inline cation removal, PFAS recovery in water samples containing 350 mg/mL of Ca^{2+} and Mg^{2+} improved from 90…115% to 93…107%.

While PFAS determination of low salt-containing water samples is best performed by straightforward direct-injection IC, water rich in alkaline-earth metals are best analyzed using Metrohm`s Inline Cation Removal.

Introduction

The rapidly expanding research on commercially important perfluorinated alkyl substances such as perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) has resulted in a wide range of analytical methods to determine their human and environmental exposure potential. LC-MS/MS is currently used for the determination of anionic perfluorinated surfactants. The analytical methods for PFAS determination in water samples generally employ a C18-SPE column, either with or without ion pairing or acidification, followed by LC-MS/MS. However, this method suffers from relatively high running and investment costs.

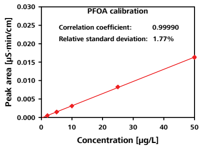
This poster presents an easy-to-use and economic direct-injection method for PFOA and PFOS determination in drinking water samples. The method is validated in terms of linearity, recovery and matrix effects. For water samples having a high cationic content, such as tap, lake, sludge or river water, an alternative method using upstream inline sample preparation is presented.

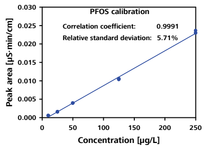
Instrumentation

- 850 Professional IC Anion – MCS – Prep 3
- 858 Professional Sample Processor

Direct injection

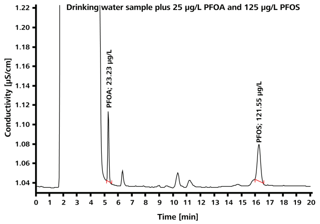
(a) Linearity





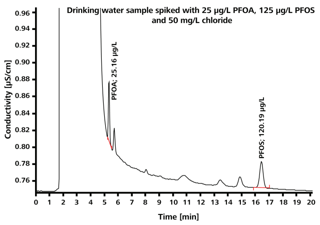
(b) Spiked drinking water sample (25 µg/L PFOA, 125 µg/L PFOS)

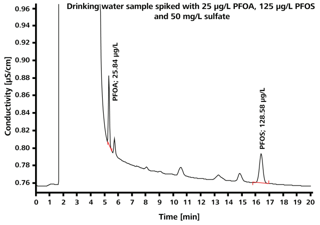
All validations were performed with PFOA- and PFOS-free drinking water samples from Kinley (Coca Cola Company) each spiked with 25 µg/L PFOA and 125 µg/L PFOS.

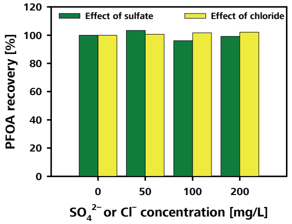


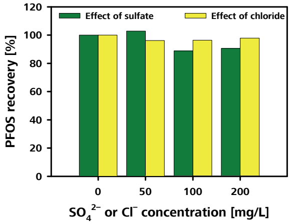
Sample:	**spiked Kinley water sample**
Column:	ProntoSil 120-5-C18 AQ
Column temp.:	35 °C
Eluent:	20 mmol/L boric acid 4.0 mmol/L NaOH (pH adjusted to 8) 38% acetonitrile
Flow:	1.0 mL/min
Loop:	1000 µL

c) Matrix influence of chloride and sulfate



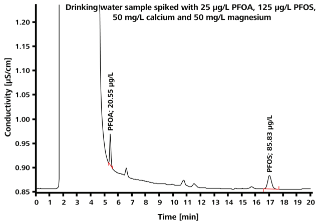




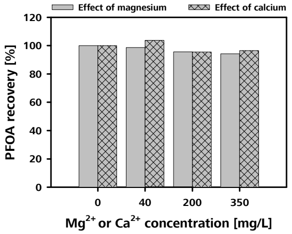


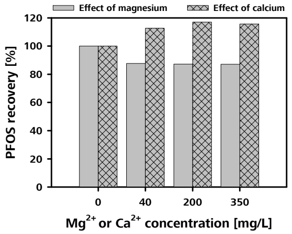
Recoveries better than 95% and 90% indicate that a sample matrix containing up to 200 mg/L chloride or sulfate has no significant influence on PFOA and PFOS quantification, respectively.

d) Matrix influence of magnesium and calcium

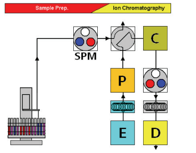


Magnesium and/or calcium concentrations above 10 mg/L significantly impair PFOS recovery and require an upstream removal of interfering cations by Metrohm`s Inline Cation Removal technique. However, samples with divalent cation concentrations smaller than the treshold value of 10 mg/L can be directly injected on the separation column.





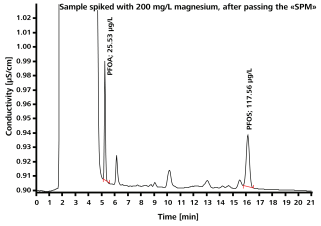
Metrohm`s Inline Cation Removal

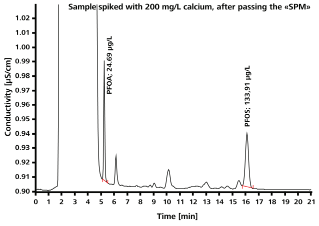


Components

- **Eluent degasser**
- **C Column**
- **Injection valve**
- **D Conductivity detector**
- **MSM II, SPM**
- **CO_2 suppressor**
- **E Eluent**
- **Sample processor**
- **P Pump**

The interfering alkaline earth metals in the sample matrix were removed by applying Metrohm`s Inline Cation Removal technique. Using Metrohm`s Sample Preparation Module «SPM», calcium and magnesium ions in the sample are automatically replaced by sodium ions.





After removal of the alkaline earth metals, recoveries for PFOA and PFOS ranged between 98.7…102.1% and 93.6…107.1%, respectively.

While PFOA and PFOS determination in low salt-containing water samples can be performed using straightforward direct-injection chromatography, samples with higher alkaline-earth-metal concentration, such as tap, lake, sludge or river water samples, should pass over the MSM cation exchanger prior to separation.

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