

DOI: <http://doi.org/10.21698/simi.2021.ab46>

NEW LC-MS/MS METHOD FOR PFOA AND PFOS DETERMINATION IN SURFACE WATER SAMPLES

Florentina Laura Chiriac, Iuliana Paun, Florinela Pirvu, Gabriel Serban, Vasile Iancu, Marcela Niculescu, Ionut Cristea, Luoana Florentina Pascu

National Research and Development Institute for Industrial Ecology-ECOIND, 57-73 Drumul Podu Dambovitei Street, district 6, 060652, Bucharest, laura.chiriac@indecoid.ro, Romania

Keywords: *endocrine disruptor, environment, LC-MS/MS, PFOA, PFOS*

Introduction

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are completely fluorinated persistent organic anions. They are synthetically produced or obtained from the degradation or metabolism of other fluorochemicals. In recent decades, PFOS and PFOA have been used in a wide variety of industrial, commercial and household applications for their high thermal and oxidative resistance and are commonly found in common products such as cleaning products, non-stick cookware, food packaging, carpets and textiles, fire-fighting foams and semiconductors. Perfluorinated compounds are bioaccumulative, toxic, endocrine disruptor and, more important, ubiquitous in both the environment and human's life. PFOS and PFOA are among the best-known endocrine disruptors, along with BPA (bisphenol A). The aquatic environment is the main most affected environmental compartment, because these compounds are released into natural receptors through discharging of industrial and municipal wastewater. For this reason, it is important to develop a sensitive, selective, versatile and reliable analytical method for the determination of perfluorinated organic compounds from various components of the environment (surface water, sediment, wastewater).

Materials and methods

The standards used were of analytical purity: perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were obtained from Sigma-Aldrich (Germany). The solvent used was: methanol - Merck (Darmstadt, Germany), and the modification of the aqueous component of the mobile phase was done using acetic acid, formic acid and ammonium acetate - Sigma-Aldrich (Germany).

Results and conclusions

The separation of the two organic pollutants was performed on a C18 chromatographic column. Chromatographic separation The optimization of the consisted in modifying the aqueous component of the mobile phase with various organic modifiers, such as formic acid and ammonium acetate. The strongest analytical signal was obtained after using the aqueous phase modified with 5mM ammonium acetate. The elution for both analytes was carried out in isocratic mode, using a low flow rate, 0.2 mL/min, favoring the analytes ionization in the electrospray source. For a good separation, three different mobile phase ratios were

tested, varying the percentage of methanol: 60% MeOH, 65% MeOH and 70% MeOH, respectively. It was observed that the 65% MeOH percentage allows both a satisfactory separation of the two analytes, maintaining a high sensitivity and a relatively short run-time (Figure 1).

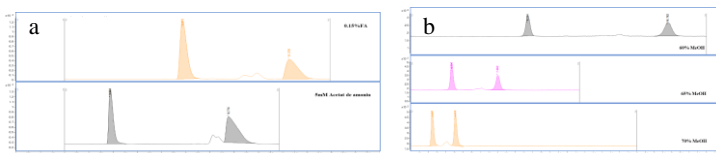


Fig.1. Chromatograms obtained after testing two organic modifiers (a) and different compositions of the mobile phase (b)

After testing the chromatographic column temperature in the range 30–46°C, it was observed that the temperature increase, the compound elution was faster but does not generate a substantial change of separation, but has a considerable influence only on the retention time for PFOS. Regarding the change of the chromatographic peak width, their variation depending with the temperature was almost imperceptible (Figure 2).

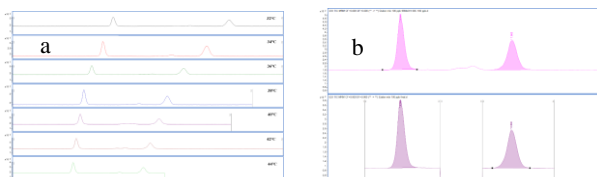


Fig. 2. Chromatograms obtained after changing the temperature of the chromatographic column (a) and using acquisition segments (b)

During the method development for determination of PFOS and PFOA from water samples, an attempt was made to obtain detection and quantification limits as low as possible to allow their determination of extremely low levels (below ng/L) at which these compounds are expected to be found in real surface water samples. Thus, all triple quadrupole MS (QQQ) detector and electrospray ionization source parameters were optimized: fragmentor voltage, collision energy, cell accelerator voltage, capillary voltage, drying gas temperature, drying gas flow and nebulizer pressure (Table 1).

Table 1. Optimized MS parameters

| Analytes | tR (min) | MRM transition | Frg (V) | CE (V) | CAV (V) | CV | Dwell time (msec) |
|----------|----------|----------------|---------|--------|---------|------|-------------------|
| PFOA | 4.23 | 412.9→368.9 | 115 | 5 | 3 | 4000 | 250 |
| | | 412.9→169.0 | 115 | 20 | 6 | | |
| PFOS | 7.14 | 498.9→80.0 | 135 | 60 | 0 | 4000 | 250 |
| | | 498.9→99.0 | 155 | 55 | 5 | | |

Acknowledgements. This study was supported by The National Research Program "Nucleu", contract no. 20N/2019, Project code PN 19 04 01 01.