Fast HPLC-TOFMS Analysis of Perfluorinated Organic Pollutants

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Introduction

In recent years, perfluorinated organic surfactants have been demonstrated to accumulate to measurable levels in fresh[1] and salt[2] water and living organisms including marine mammals[3] and humans.[4] While widespread use of these perfluorinated compounds (PFCs) in industrial products such as fire retardants, insecticides, lubricants, adhesives, paints and polishes has resulted in their introduction into the environment, the lack of appropriate metabolic or degradation pathways has led to their continued accumulation. Although a major producer of PFCs has discontinued production of these chemicals there is still little known about the toxicology of PFCs and fears that these compounds may continue to rise to dangerous levels are increasing. In an effort to study the impact of PFCs on the environment fast analytical methods to detect and quantify these compounds at trace levels are required.

Trace analysis of target PFCs down to sub picogram levels has been accomplished using HPLC combined with tandem MS/MS techniques.1-4 The drawback of these methods however, is that the analysed compounds must be known prior to analysis. Time-of-flight mass spectrometry (TOFMS), on the other hand, can provide high sensitivity (in the low pg range) for all compounds within a sample and so allows for detection of both known and unknown compounds. Low ppm mass accuracy can also aid identification through molecular formula calculation and the wide dynamic range provided by modern TOFMS instrumentation can provide useful quantitative information. Another benefit afforded by TOFMS is the ability to acquire data at fast acquisition speeds. This allows for proper identification of even the narrowest of chromatographic peaks which means high speed chromatographic techniques may be used to reduce analysis time. As an example, using HPLC columns packed with <2mm sized particles, 2-5 fold reductions in analysis time over traditional columns are routinely observed. In this work, a fast chromatographic method is developed to separate 7 perfluorinated compounds. To match the fast chromatographic speed, fast and sensitive detection of these compounds is achieved using negative mode ESI-TOFMS. Through the use of isotopically labeled internal and external standards, quantitative results are obtained for all compounds.

Instrumentation

Agilent 1100 vacuum degasser, Gilson 321 binary gradient pump module and 215 liquid handler, LECO Corporation Unique® LC-TOFMS with ESI Source and ChromaTOF® software

LC Method

5.00min run time

0.400 mL/min flow rate

2.1mm x 50mm, 1.8mm ZorbaxStableBond C18 Rapid Resolution Column

Mobile phase A: 10mM aqueous ammonium acetate; Mobilephase B: MeCN

Gradient: 0.00min, 10%B; 0.50min, 10%B; 2.50min, 95%B; 5.00min, 95%B

Injection volume: 10mL

MS Method

ESI voltage -500V

Desolvation temperature 210 ºC

Desolvation gas (N2) 6.0 L/min

Nebulizer pressure 200kPa

Interface temperature 100 ºC

Nozzle -95V

Acquisition rate 4.17 spectra/second

Standards

Perfluoro-1-octanoic acid (PFOA), perfluoro-1-octanesulfonic acid (PFOSA), perfluoro-1-heptanoic acid (PFHA) and perfluoro-1-decanoic acid (PFDA) were obtained from Sigma-Aldrich.

2H-perfluoro-2-decenoic acid (FOUEA), perfluoro-1-octanesulfonamide (FOSA) and N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA) were obtained from Wellington Labs (Guelph, Ontario Canada).

Mass labeled standards:

Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid (MPFOA), perfluoro-n-[1,2-$^{13}C_2$]decanoic acid, 2H-perfluoro-[1,2-$^{13}C_2$]-2-decenoic acid and N-ethyl-d_5-perfluoro-1-octanesulfonamide (d-N-EtFOSA) were obtained from Wellington Labs (Guelph, Ontario Canada).

Results

Using a standard mixture of the 7 PFCs at 100ng/mL separation was achieved in under 5 minutes using the small particle size column and fast gradient method (Figure 1). Mass accuracies were measured to be <10ppm using an external calibration with Agilent Tune mix (2-pt calibration with m/z 112.9855 and 601.9790). From the response of the 100ng/mL standards injection the detection limits for the PFCs was estimated to be in the range from 0.42 ng/mL for PFOSA to 2.9 ng/mL for FOUEA (estimated by linear extrapolation to S/N = 3:1). Quantitative data will be demonstrated by spiking the standard mixture with the mass labeled standards. This will provide internal standards for four of the seven compounds and the remaining three compounds will be determined semi-quantitatively using the most appropriate mass labeled spiked standard.

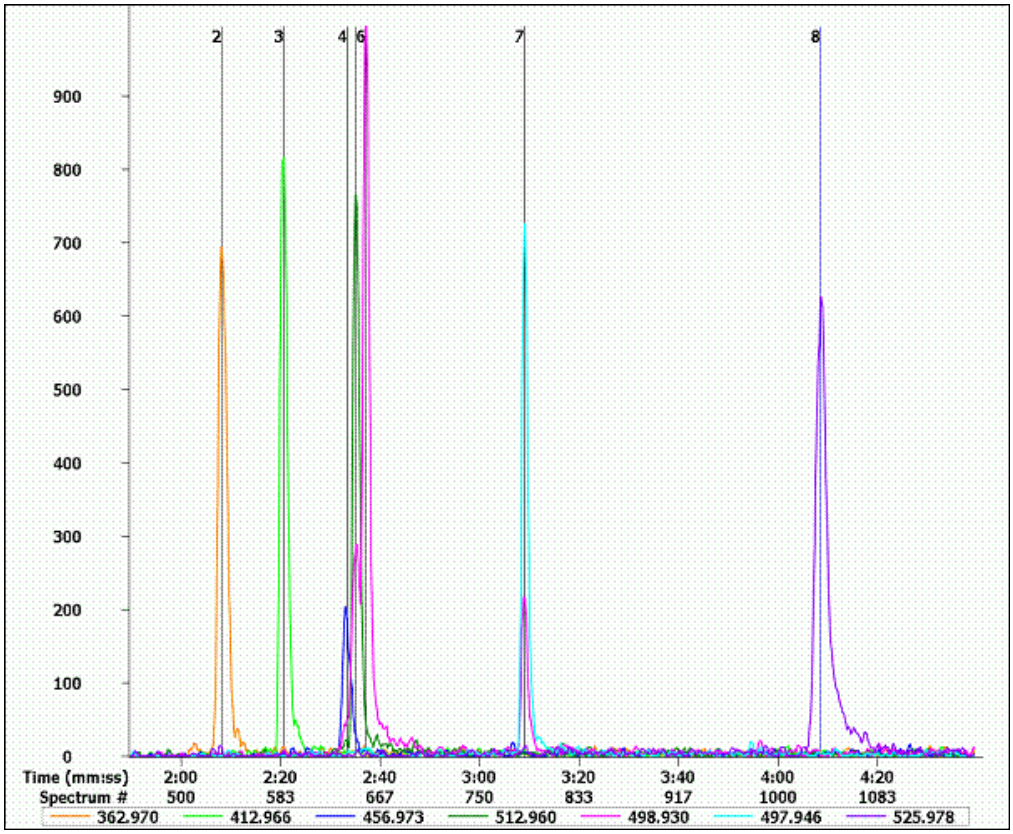

Figure 1. Fast separation of 7 PFCs and detection by TOFMS.

Conclusion

Separation of 7 PFCs was accomplished in under 5 minutes using a fast LC-TOFMS method. Good mass accuracy and high sensitivity was achieved using a TOFMS as the detector.

References

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