

Analysis of Perfluorochemicals (PFOA, PFOS) using LC-MS

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are organofluorine compounds that consisting of chains of 7 and 8 carbons, respectively, with fluorine atoms bonded to each carbon, and a carboxyl group and sulfonate group, respectively, at the end of the chain. Because they possess a hydrophilic functional group and hydrophobic alkyl side chain, they are readily soluble in both water and oil. With that type of property, PFOA, PFOS and related substances have been widely used in industrial products as surface-active agents, water-repellents and waterproofing agents, etc. Recent research efforts have confirmed their accumulation in the human body and in wild animals, and remain in the

environment on a global scale since the bond between carbon atoms and fluorine atoms is extremely strong and creates a highly stable compound. Although their biological toxicity is still not fully clarified, they are receiving attention as new persistent organic pollutants.

Here we introduce a simultaneous analysis of typical PFOA and PFOS compounds using LC-MS. Fig.1 shows the negative ESI mass spectra of PFOA and PFOS. Depronated molecules are observed at m/z 413 and 499, respectively. Fig.2 shows the total ion chromatogram and mass chromatogram of a standard solution.

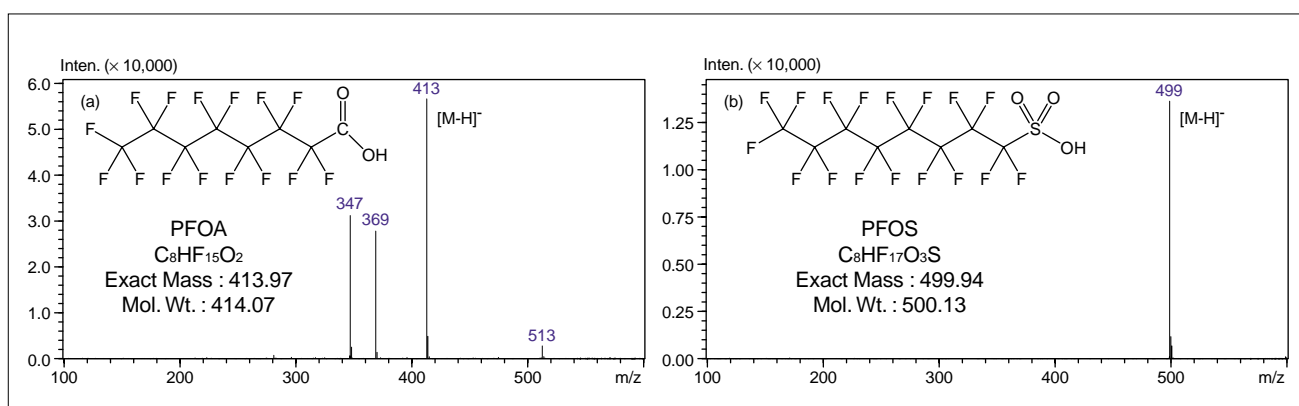


Fig.1 ESI Mass Spectra of PFOA (a) and PFOS (b)

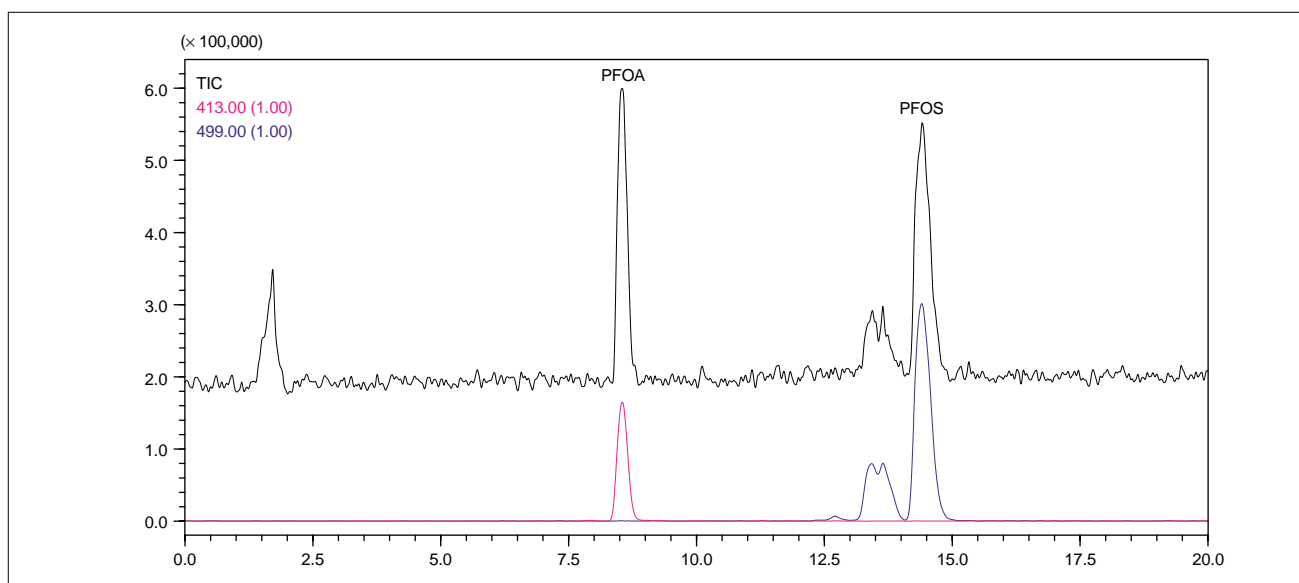


Fig.2 Total Ion Chromatogram and Mass Chromatogram of PFOA and PFOS (each 1 mg/L)

Fig.3 shows a 6-point calibration curve (0.1 to 50 µg/L). Excellent linearity is achieved for both compounds in this concentration range, with both the coefficient of correlation and coefficient of determination greater than 0.9999. In addition, from the excellent repeatability (n=5) obtained (Table 1, 2), it is clear that high sensitivity analysis is possible using LC-MS.

Now, in order to reduce contamination due to PFOA,

careful attention is required in handling solvents (commercial LC-MS solvents) used in the preparation of the mobile phase and sample, and in handling glassware. Moreover, to avoid solving out of PFOA from fluororesins used in the LC system, the mobile phase was degassed offline rather than using an online degasser, and all flow line tubing made of fluororesin was replaced with PEEK tubing to conduct this analysis.

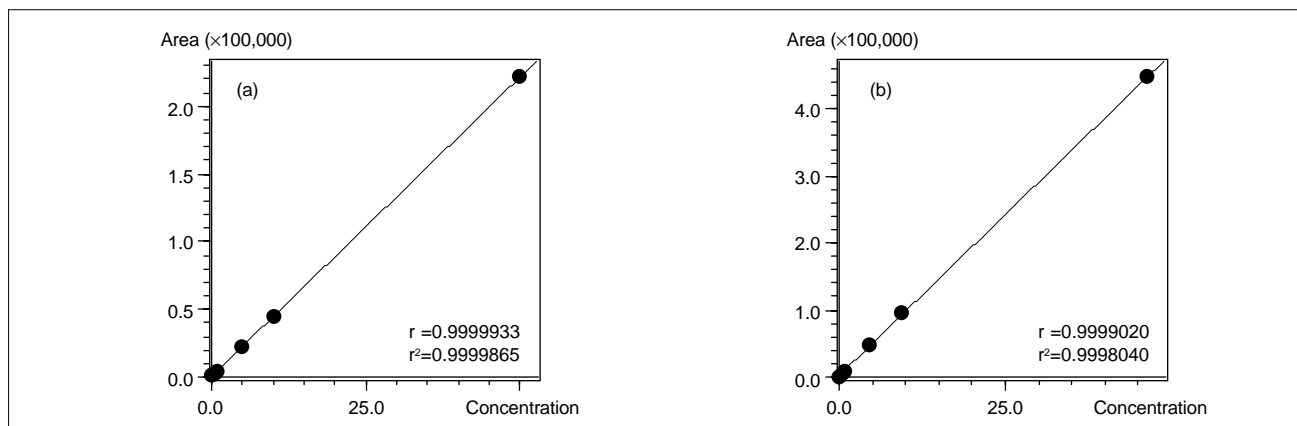


Fig.3 Calibration curve of PFOA (a) and PFOS (b).

Table 1 Repeatability of Peak Area of PFOA (*m/z* 413)

| Conc. (µg/L) | 1st | 2nd | 3rd | 4th | 5th | Average | Standard Deviation | %RSD |
|--------------|--------|--------|--------|--------|--------|---------|--------------------|-------|
| 0.1 | 994 | 669 | 445 | 626 | 814 | 710 | 206 | 29.09 |
| 0.5 | 2544 | 2544 | 2671 | 2356 | 2581 | 2539 | 115 | 4.52 |
| 1 | 4766 | 4861 | 4591 | 4498 | 4576 | 4658 | 150 | 3.21 |
| 5 | 23092 | 23574 | 22134 | 22768 | 22553 | 22824 | 545 | 2.39 |
| 10 | 44902 | 45143 | 44960 | 44871 | 46270 | 45229 | 591 | 1.31 |
| 50 | 218423 | 224210 | 221993 | 220259 | 222012 | 221379 | 2167 | 0.98 |

Table 2 Repeatability of Peak Area of PFOS (*m/z* 499)

| Conc. (µg/L) | 1st | 2nd | 3rd | 4th | 5th | Average | Standard Deviation | %RSD |
|--------------|--------|--------|--------|--------|--------|---------|--------------------|------|
| 0.09 | 1036 | 1148 | 1223 | 1038 | 1129 | 1115 | 79 | 7.11 |
| 0.47 | 4921 | 5288 | 4856 | 5286 | 5580 | 5186 | 298 | 5.74 |
| 0.93 | 9690 | 9782 | 10280 | 10160 | 9346 | 9852 | 376 | 3.82 |
| 4.65 | 48977 | 48215 | 48614 | 47895 | 46993 | 48139 | 759 | 1.58 |
| 9.29 | 95648 | 96583 | 96178 | 95826 | 95206 | 95888 | 523 | 0.55 |
| 46.46 | 451014 | 445768 | 450017 | 445595 | 446550 | 447789 | 2540 | 0.57 |

Table 3 LC-MS Analytical Conditions

| | | | |
|--------------------------|---|--------------------------|----------|
| Column | : Shimadzu Shim-pack FC-ODS (2.0 mmI.D. × 150 mmL.) | | |
| Mobile phase A | : 5 mmol/L Ammonium acetate - Water | | |
| Mobile phase B | : Acetonitrile | | |
| Time program | : 35 %B (0 min)→50 %B (7.5 -12 min)→90 %B (20 min)→35 %B (20.01 min) →STOP (30 min) | | |
| Flow rate | : 0.2 mL/min | | |
| Injection volume | : 10 µL | Column temperature | : 40 °C |
| Probe voltage | : -3.5 kV (ESI-Negative mode) | Block heater temperature | : 200 °C |
| CDL temperature | : 250 °C | | |
| Nebulizing gas flow | : 1.5 L/min | | |
| CDL voltage | : using Default value | | |
| Q-array DC & RF voltages | : using Default values | | |
| Drying gas pressure | : 0.1 MPa | | |
| Scan range | : <i>m/z</i> 100-600 | | |
| SIM | : <i>m/z</i> 413 for PFOA (Segment 1 : 0-12 min), <i>m/z</i> 499 for PFOS (Segment 2 : 12-30 min) | | |

NOTES:

*This Application News has been produced and edited using information that was available when the data was acquired for each article. This Application News is subject to revision without prior notice.



SHIMADZU CORPORATION. International Marketing Division

3, Kanda-Nishikicho 1-chome, Chiyoda-ku, Tokyo 101-8448, Japan Phone: 81(3)3219-5641 Fax: 81(3)3219-5710
Cable Add.: SHIMADZU TOKYO