

Simultaneously Direct Analysis of 17 Perfluorinated Compounds by a New Generation Triple Quadrupole LC / MS System TSQ Altis

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ABSTRACT

Purpose: To demonstrate a direct injection method for the analysis of 17 perfluorinated compounds by the Thermo Scientific™ TSQ Altis™ Triple Quadrupole Mass Spectrometer.

Methods: Take 1mL of water sample (drinking water and groundwater) in a 1.5mL centrifuge tube, centrifuge at 12000 rpm for 5min, and then take the supernatant through a 0.22µm water filter. Then SRM data was acquired for qualitative and quantitative multi PFCs using liquid chromatography (UPLC) coupled to the TSQ Altis mass spectrometer.

Results: The detection limit (LOD) of all 17 perfluorinated compounds is between 1 ~ 10 pg / mL and the limit of quantification (LOQ) is between 2 ~ 20 pg / mL. The sensitivity of each compound fully meets the requirements of EPA 537.

INTRODUCTION

The Perfluorinated compounds (PFCs) are a class of artificial compounds with special chemical properties. PFCs have C-F bonds with strong bond energy, and their great stability makes these compounds difficult to chemically and biodegrade in environmental media, and can be amplified and enriched in the body. In this paper, a direct injection method for the analysis of 17 perfluorinated compounds by TSQ Altis was established. This method has high selectivity, fast analysis speed, sensitivity fully meets regulatory requirements, and has good reproduction and wide linear range. The analysis results of the actual environmental matrix samples are satisfactory, which can be used for rapid and accurate quantitative analysis of trace PFCs in environmental waters.

MATERIALS AND METHODS

Sample Preparation

All 17 perfluorinated compounds (MPFACs-MXB) and 9 internal standards (MPFACs-MXA) were purchased from Wellington (see table 1 for the list of compounds). 1mL of water sample (drinking water and groundwater) were centrifuge at 12000 rpm for 5min in a 1.5mL centrifuge tube, and then take the supernatant through a 0.22µm water filter.

Test Method(s)

A Thermo Scientific™ Vanquish™ UHPLC and TSQ Altis mass spectrometer were used for data acquisition. Chromatography analysis was carried out by a C18 Trap column (Thermo Scientific™ Accucore™, 50 mm × 2.1mm, 2.6 µm) and a C18 analysis column (Thermo Scientific™ Accucore aQ™, 100 mm × 2.1mm, 2.6 µm) with H₂O containing 10 mmol/L ammonium acetate solution (A) and methanol (B) as the mobile phase in gradient elution program (Table 2). The flow rate was set at 0.30 mL / min. The injection volume was set at 10 µL.

A H-ESI II source was coupled to a TSQ Altis Triple quadrupole mass spectrometer. Source conditions were set as: negative mode; spray voltage: 3000 V; sheath Gas: 50 arb; AUX gas: 10 arb; auxiliary gas temperature: 400 °C; ion transmission tube temperature: 320 °C. Q1 resolution: 0.7; Q3 resolution: 0.7; CID collision energy: 2.0 mTorr. Acquisition mode: SRM (table 1).

Data Analysis

Thermo Scientific™ Xcalibur™ platform was used for data analysis. Thermo Scientific™ QualBrowser™ and Freestyle™ software was used for initial spectra viewing while Thermo Scientific™ TraceFinder™ for quantification.

Table 2. Gradient elution program for multi pesticide residues analysis

Time (min)	A%	B%
0.0	80	20
1.5	60	40
9.0	5	95
12.0	5	95
12.1	80	20
15.0	80	20

Table 1. 17 Perfluorinated Compounds and 9 Internal Standard SRM Parameters

Compound	RT (min)	Precursor (m/z)	Product (m/z)	Collision Energy (V)	Min Dwell Time (ms)	RF Lens (V)
PFBA	3.23	212.9	168.988*	10.23	98.667	30
PFBA	3.23	212.9	194.929	11.44	98.667	30
¹³ C ₄ -PFBA	3.23	216.993	172	9	98.667	30
PFPeA	5.12	262.868	218.887*	10.23	73.786	30
PFPeA	5.12	262.868	244.875	10.23	73.786	30

PFBS	5.42	298.87	79.917*	32.59	58.599	78.74
PFBS	5.42	298.87	98.988	28.42	58.599	78.74
PFHxA	6.33	312.87	118.917	18.72	35.992	30
PFHxA	6.33	312.87	268.988*	10.23	35.992	30
¹³ C ₂ -PFHxA	6.33	314.99	269.988	10.23	35.992	30
PFHpA	7.18	362.9	168.988	15.72	35.992	32.78
PFHpA	7.18	362.9	318.917*	10.23	35.992	32.78
PFHxS	7.24	398.888	79.946*	37.37	35.992	79.86
PFHxS	7.24	398.888	98.917	32.71	35.992	79.86
¹⁸ O ₂ -PFHxS	7.24	402.888	83.946	37.37	35.992	80
PFOA	7.84	412.87	168.988	16.14	23.408	33.71
PFOA	7.84	412.87	368.917*	10.23	23.408	33.71
¹³ C ₄ -PFOA	7.84	416.9	371.917	16.14	23.408	34
PFNA	8.38	462.868	218.917	15.08	18.415	39.64
PFNA	8.38	462.868	418.988*	10.23	18.415	39.64
¹³ C ₅ -PFNA	8.38	467.868	422.988	12	18.415	40
PFOS	8.38	498.85	79.917*	40.44	18.415	78.74
PFOS	8.38	498.85	98.917	38.17	18.415	78.74
¹³ C ₄ -PFOS	8.38	502.85	79.917	40.44	18.415	79
PFDA	8.83	512.87	268.917	15.31	18.415	47.05
PFDA	8.83	512.87	468.988*	10.23	18.415	47.05
¹³ C ₂ -PFDA	8.83	514.87	469.988	10.23	18.415	47
PFDS	9.18	598.85	79.917*	44.65	18.415	83.38
PFDS	9.18	598.85	98.917	42.87	18.415	83.38
PFUDA	9.21	562.85	268.917	16.37	18.415	52.24
PFUDA	9.21	562.85	318.958	15.91	18.415	52.24
PFUDA	9.21	562.85	518.917*	10.23	18.415	52.24
¹³ C ₂ -PFUDA	9.21	564.85	519.917	12	18.415	52
PFDoA	9.53	612.87	318.958	17.09	18.479	55.39
PFDoA	9.53	612.87	568.917*	10.23	18.479	55.39
¹³ C ₂ -PFDoA	9.53	614.89	569.917	10.23	18.479	55
PFTrDA	9.8	662.87	318.958	18.07	18.479	58.73
PFTrDA	9.8	662.87	368.857	17.85	18.479	58.73
PFTrDA	9.8	662.87	618.917*	10.23	18.479	58.73
PFTeDA	10.05	712.92	368.917	18.8	19.945	63.55
PFTeDA	10.05	712.92	668.958*	10.23	19.945	63.55
PFHxDA	10.46	812.9	318.929	21.68	28.559	83.56
PFHxDA	10.46	812.9	768.917*	11.33	28.559	83.56
PFODA	10.79	912.868	618.887	21.34	28.649	78.19
PFODA	10.79	912.868	868.917*	12.2	28.649	78.19
PFODA	10.79	912.868	887.679	10.57	28.649	78.19

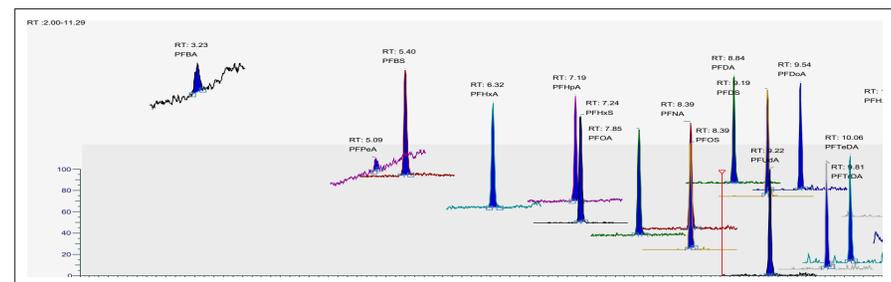


Figure 1. Chromatography Overlay of 17 PFCs (20pg/mL)

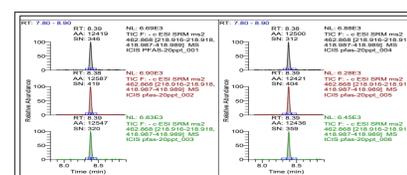


Figure 2. The representative compound PFBA was injected for 6 consecutive injections (RSD=0.6%)

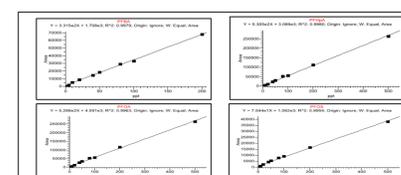


Figure 3. Standard curves of representative compounds PFBA, PFHpA, PFOA and PFOS in mixed standards

RESULTS AND DISCUSSIONS

Optimization of Mass Spectrometry Conditions

Seventeen perfluorinated compounds and their internal standard mass spectrometry parameters were optimized by "T" tee. Tune software can monitor the signal intensity and spray stability of various compounds, and can realize automatic simultaneous optimization of ion source parameters such as sheath gas, auxiliary gas, spray voltage, RF Lens, collision energy, etc. Finally, the optimal mass spectrum conditions of all compounds can be obtained.

Sensitivity, Linearity and Precision

The detection limit LOD of all compounds is between 1 and 10 pg/mL, the quantitative limit LOQ is between 2 and 20 pg/mL, and the sensitivity of each compound completely meets the requirements of EPA 537. Fig. 1 is chromatogram of 17 PFCs at a concentration of 20 pg/mL. The mixed standard of 20 pg/mL is continuously injected for 6 times, and the reproducibility of peak area is ≤5.1% all. Fig. 2 is a chromatogram of representative compound PFNA for 6 injections continuously. All compounds showed good linear relationship in the concentration range of 2-500 pg/mL, with linear correlation coefficient $r > 0.99$. Fig. 3 is a linear plot of several typical compounds.

Environmental water analysis

The analysis of drinking water (tap water from the Beijing Wangjing Laboratory of ThermoFisher Scientific (China)) and groundwater (groundwater from Hebei Province of China) showed that PFOA was detected in the former and not in the latter. Groundwater was selected as blank substrate with an addition concentration of 20 pg/mL. After 6 consecutive injections, RSD of peak area reproducibility of 17 PFCs were ≤6.3%. Fig. 4 is extracted ion chromatograms with 20 pg/mL mixed standard added to the matrix.

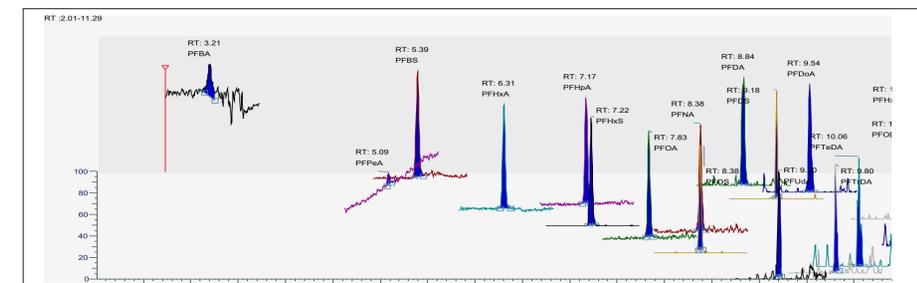


Figure 4. Chromatography Overlay of 17 PFCs (20pg/mL spiked samples)

CONCLUSIONS

- A method for simultaneous determination of 17 perfluorinated compounds in environmental water by direct injection was established.
- All compounds showed good linear relationship in the concentration range of 2-500 pg/mL, with linear correlation coefficient $r > 0.99$.
- The sensitivity of each compound completely meets the requirements of EPA 537.
- The reproducibility and sensitivity are very good in the detection of spiked samples.
- The method is completely suitable for rapid and efficient monitoring and analysis of organic pollutants such as PFCs in the environment.

TRADEMARKS/LICENSING

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