Application News

Suppressor Ion Chromatograph HIC-ESP

Analysis of AOF (Adsorbable Organic Fluorine) According EPA Method 1621

Tomoka Kaseda[1], Shunsuke Goto[2]
1 Shimadzu Corporation, 2 Nittoseiko Analytech

User Benefits

- The combination of the combustion unit and IC can perform AOF analysis according EPA Method 1621.
- AOF analysis is a simplified and useful technique for screening PFAS.
- The CIC system enables automation of the entire process from sample combustion to ion chromatography analysis.

■ Introduction

The US Environmental Protection Agency (USEPA) has published Method 1621[1)], a screening method for the determination of AOF in aqueous matrices by combustion Ion chromatograph (CIC). This method detects organic fluorine compounds that are dissolved in water. The common sources of organic fluorine compounds are PFAS and non-PFAS fluorinated compounds such as pesticides and pharmaceuticals.

AOF compounds in the sample are adsorbed on a granular activated carbon (GAC) and decomposed by combustion. The generated combustion gas is collected in an absorbing solution and analyzed for fluoride by ion chromatography. An advantage of this technique is that it provides information on the total amount of PFAS that may not be targeted by other selective chromatography methods.

In this application news, we introduce the analysis of AOF with CIC. Perfluorohexane sulfonic acid (PFHxS), the prescribed spiking compound in EPA Method 1621, was evaluated for initial precision and recovery (IPR).

■ Experimental

The Shimadzu HIC-ESP ion chromatograph was equipped with the Nittoseiko Analytech Co., Ltd. AQF-2100H combustion unit (Fig.1). The sample preparation and analysis process are summarized below.

1. The sample is passed through the TXA-04 absorption unit. (Nittoseiko Analytech Co., Ltd.)
2. GAC column is rinsed to remove inorganic fluorine.
3. GAC is transferred to the ceramic boat and combusted
4. Combustion products are captured in the absorption solution
5. Absorption solution is analyzed by Ion chromatography

Table 1 shows the analytical conditions for combustion and chromatography.

Table 1 Analysis Conditions for AQF-5000H and HIC-ESP

System	: AQF-5000H
Sample boat	: Ceramic
Pyrolysis tube	: Ceramic inner + quartz outer tube
Furnace inlet temperature	: 1000 ° C
Furnace outlet temperature	: 1100 ° C
Oxygen flow	: 400 mL/min
Argon flow	: 200 mL/min
Humidified argon flow	: 100 mL/min
Absorption solution	: Reagent Water
Final absorption solution volume	: 11.3 mL

System	: HIC-ESP
Column	: Shim-pack™ IC-SA2[*1] (250 mm × 4.0 mm I.D., 9 µm)
Mobile phase	: 0.6 mmol/L Na_2CO_3 12 mmol/L $NaHCO_3$
Flow rate	: 1.0 mL/min
Column temperature	: 30 ° C
Injection volume	: 50 µL
Suppresoe unit	: ICDS™-40A
Detection	: Conductivity

[*1] P/N: 228-38983-91

Fig.1 Combustion ion chromatograph
AQF-5000H automatic sample combustor manufactured by Nittoseiko Analytec Corporation (right) and HIC-ESP electrodialysis suppressor ion chromatograph manufactured by Shimadzu Corporation (left)

■ Combustion calibration curve

EPA 1621 requires calibration standards go through combustion but not through the carbon. In this analysis, sodium fluoride solution was used as the standard solution, and 200 µL of the standard solution was combusted and absorbed in 11.3 mL of ultrapure water. The chromatogram of the 1.8 µg/L standard solution used in the combustion calibration curve is shown in Fig. 2. Phosphoric acid standard solution was used as the internal standard.

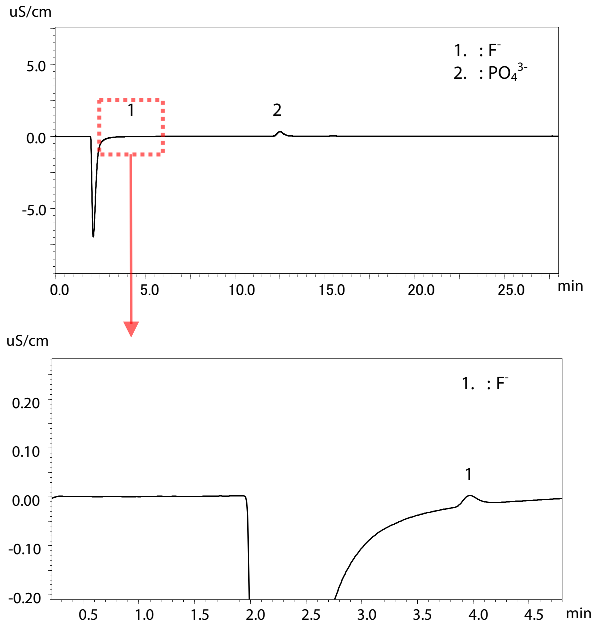

Fig. 2 Chromatogram of Sodium Fluoride Standard Solution (1.8 µg/L)
(Lower: Enlarged Chromatogram in the Vicinity of Fluoride Ion)

A six point calibration curve was prepared from the analysis results of standard solutions with fluoride ion concentrations between 1.8 µg/L and 442.5 µg/L. The resulting calibration curve is shown in Table 2. The calibration curve was prepared using a quadratic equation, and measured concentrations of each calibration point was within 80-120% according to EPA 1621. Table 2 shows the accuracy (%) of each calibration point concentration and the calculated concentrations.

Table 2 Concentrations at each calibration point and accuracy (%)

Normal concentration (µg/L)	Area	Measured concentrations (µg/L)	Accuracy (%)
1.8	198	2.04	113.2
8.8	663	8.79	99.9
17.7	1,265	17.5	99.1
88.5	6,154	88.3	99.8
177.0	12,332	177.2	100.1
442.5	31,031	442.5	100

The RSE (Relative Standard Error) was calculated according to the procedure described below. The RSE was 7.7%, which was confirmed to be less than 20%.

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \frac{\left[\frac{x'i - xi}{xi}\right]^2}{n-p}}$$

x_i: Normal concentration (true value) of each calibration standard

x'_i: Measured concentration of each calibration standard

n: Number of standard levels in the curve

p: Type of curve (2=linear,3=quadratic)

■ Method Blank (MB)

In order to determine the presence of fluoride ion contamination from reagents and instruments involved in the pretreatment process, 100 mL of ultrapure water was passed through GAC, and analyzed according to the method.

Fig. 3 shows the chromatogram of the method blank.

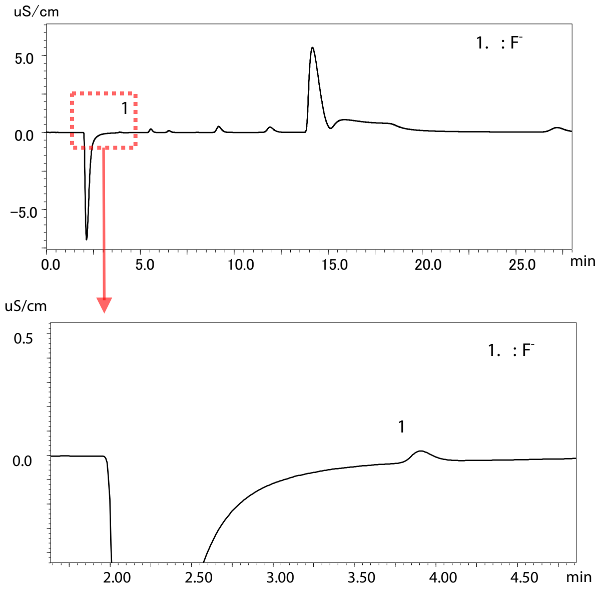

Fig. 3 Method Blank Chromatogram
(Lower: Enlarged Chromatogram in the Vicinity of Fluoride Ion)

The AOF concentration (µg/L) in the blank was calculated according to the procedure described in EPA 1621. The formula is shown below.

$$\text{AOF } (\mu g/L) = C_{MB} \times \frac{V_{abs}}{V_{MB}}$$

AOF: Concentration of AOF contained in 1L of sample (µg/L)

C_{MB}: measured concentration of the method blank (µg/L)

V_{abs}: volume of the absorbing solution (mL)

V_{MB}: volume of method blank passed through activated carbon (mL)

Table 3 shows the mean values of repeatability and quantitative results of four consecutive analyses of method blanks. The method blank was confirmed to be less than 4.0 µg/L, which is specified in EPA 1621.

Table 3 Quantitative Results of Method Blanks

	Result	Criteria
Method Blank (µg/L)	0.60	< 4.0

■ Initial Precision and Recovery (IPR)

Four aliquots of ultra pure water were spiked at 25 µg/L PFHxS as fluoride ion. Fig. 4 shows the chromatogram of the PFHxS standard solution. Table 4 shows the results of Average Recovery (%) and Repeatability (%RSD) in four consecutive analyses of PFHxS standard solutions.

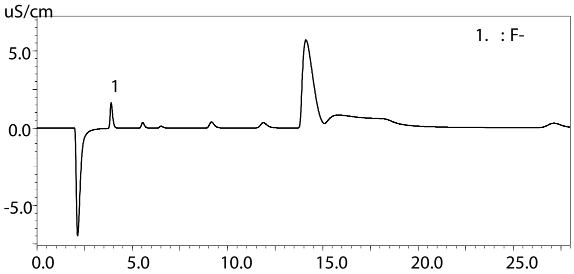

Fig. 4 Chromatogram of 25 µg/L PFHxS Standard Solution

Table 4 IPR Calculation Results

	Result	Criteria
Average Recovery (%)	95.5	80-120
% RSD	2.42	< 20

■ Method Detection Limit (MDL)

The MDL was calculated in accordance with 40 CFR Appendix B to Part 136. The MDL^b was calculated from the seven replicates over the period of three days of the method blank, and the MDL^S was calculated from the seven replicates over the period of three days of the PFHxS standard solution at 25 µg/L. The formulas used to calculate MDL^b and MDL^S are shown below.

$$MDL^S=t^{(n-1,1-\alpha=0.99)}S^S$$

MDL ^{S}: MDL calculated from the spiked sample

t $^{(n-1,\,1-\alpha=0.99}$):t-value of degrees of freedom (n-1) for one-tailed test (99%)

S^S: standard deviation for multiple analyses of added samples

$$MDL^b=x+t^{(n-1,1-\alpha=0.99)}S^b$$

MDL^b: MDL calculated from method blank analysis

x: Average value of method blanks

t $^{(n-1,\,1-\alpha=0.99)}$: t-value of degrees of freedom (n-1) for one-tailed test (99%)

S^b: standard deviation for multiple analysis of method blanks

MDL^b and MDL^S were calculated and shown in Table 5. The MDL was determined as 1.27 µg/L since MDL^S is greater than MDL^b.

Table 5 MDL

	MDL (µg/L)
MDL^b	0.97
MDL^S	1.27

■ Summary

This Application News demonstrates the analysis of AOF using the Shimadzu HIC-ESP Ion Chromatograph equipped with the Nittoseiko Analytech Co., Ltd. AQF-5000H Combustion unit.

IPR and MDL were obtained using PFHxS, and the results were within the criteria of EPA Method 1621.

<References>

1) EPA 1621 Screening Method for the Determination of AOF in Aqueous Matrices by CIC

2) 40 CFR Appendix B to Part 136 - Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 2

01-00786-EN First Edition: Feb. 2025