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Suppressor Ion Chromatograph HIC-ESP

Application News

Analysis of Adsorbable Organic Fluorine (AOF) by Combustion Ion Chromatography(CIC)

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User Benefits

- The combination of the combustion unit and IC can perform AOF analysis according EPA Draft 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 Draft Method 1621, a screening method for the determination of AOF in aqueous matrices by CIC[1]. This method detects organic fluorine compounds that are dissolved in water and adsorbed by passing the sample through a column of granular activated carbon (GAC). The common sources of organic fluorine compounds are PFAS and non-PFAS fluorinated compounds such as pesticides and pharmaceuticals.

CIC system, AOF compounds adsorbed on the GAC from the sample are decomposed by combustion. The generated combustion gas containing fluorine is collected in an absorbing solution and analyzed 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 article, we introduce the analysis of AOF with CIC. Perfluorohexane sulfonic acid (PFHxS), the prescribed spiking compound in EPA Draft Method 1621, was evaluated for determining the initial precision and recovery (IPR) and a river water sample analyzed.

■ 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 is transferred to the ceramic boat and combusted
3. Combustion products are captured in the absorption solution
4. Absorption solution is analyzed by Ion chromatography

The Draft Method 1621 states that laboratory water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents should be analyzed as method blank. Also, at least two method blanks must be analyzed at the beginning and end of each batch to ensure the absence of contamination.

Table 1 shows the analytical conditions for combustion and chromatography.

Table 1 Analysis Conditions for AQF-2100H and HIC-ESP

System	: AQF-2100H
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	: 10.3 mL

System	: HIC-ESP
Column	: Shim-pack™ IC-SA2*1 (4.0 mm × 250 mm I.D., 9 µm)
Mobile phase	: 1.8 mmol/L Na_2CO_3 1.7 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
Nittoseiko Analytech Co., Ltd. AQF-2100H Combustion unit(right) with Shimadzu HIC-ESP Ion Chromatograph(left)

■ Calibration

A 5-point calibration curve was prepared using the analysis results of five anion-mixed standard solutions with concentrations ranging from 0.01 mg/L to 0.5 mg/L. The correlation coefficient was 0.999 or higher for all components. Fig.2 shows a chromatogram of the mixed anion standard.

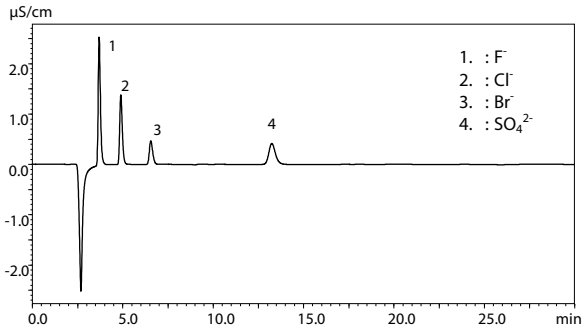

Fig.2 Chromatograms of each 0.5 mg/L mixed anionic standard solution

■ Initial Precision and Recovery (IPR)

Six 100 mL reagent water replicates spiked with PFHxSNa solution to 19.5 µg/L as fluoride ion and two method blanks were extracted and analyzed by CIC. The average concentration of the two method blanks concentration (1.6 µg/L) was subtracted from each of the six spiked samples to calculate the IPR. IPR is evaluated by calculating the average perecent recovery and the relative standard deviation (RSD) of concentration. Fig.3 shows the chromatogram of a PFHxS standard solution and Table 3 provides the results of the IPR along with the EPA Draft Method 1621 acceptance criteria.

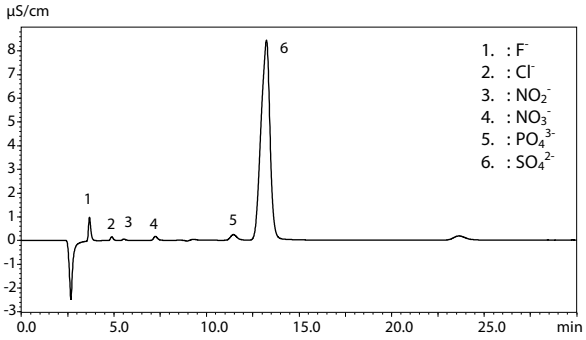

Fig.3 Chromatogram of PFHxS Standard Solution

Table 3 IPR results and acceptance criteria

	Result	Criteria
Average Recovery (%)	93.0	70-130
RSD	8.30	< 20
Method Blank (µg/L)	1.6	< 3.0

■ Analysis of river water

100 mL of river water was extracted and analyzed. The results are shown in Table 4. The average of the two method blanks concentration (1.4 µg/L) was subtracted from a river water sample. Fig.4 and 5 show an example chromatogram of the river water sample with trace anions detected, including fluoride.

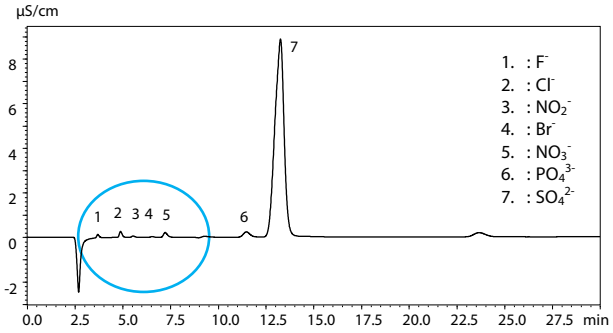

Fig.4 An example chromatogram of the river water sample

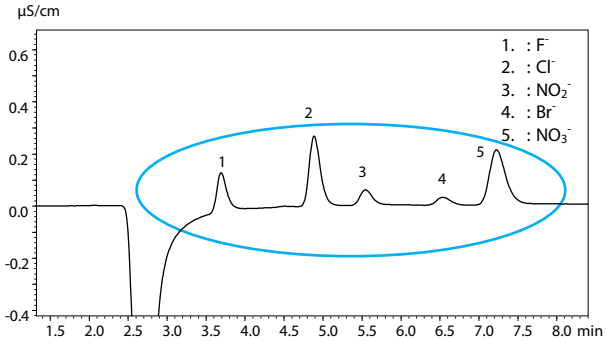

Fig.5 Enlarged example chromatogram of Fig.4

Table 4 Results of River Water Sample

	Result (µg/L)
River Water Sample	1.6

■ Conclusion

This Application News demonstrates the analysis of AOF using the Shimadzu HIC-ESP Ion Chromatograph equipped with the Nittoseiko Analytech Co., Ltd. AQF-2100H Combustion unit. Excellent recovery and precision were acheived in the IPR test using PFHxS as described in the EPA Draft Method 1621. Analysis of a river water sample demonstrates detection at the part per billion level is possible.

<References>

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

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