

## Application News

Ion Chromatograph Nexera™ IC

### Analysis of Adsorbable Organic Fluorine (AOF) in Accordance with EPA 1621 Using Combustion Ion Chromatograph (CIC) —Efficient Workflow Using C-IC Solution—

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#### User Benefits

- ◆ Entire process—from sample combustion to analysis—can be performed automatically by combination use of AQF-5000H automatic quick furnace and Nexera IC ion chromatograph.
- ◆ Integrated C-IC Solution software enables integrated operation of the combustion ion chromatograph and analysis in accordance with EPA 1621.

#### ■ Introduction

The U.S. Environmental Protection Agency has published EPA 1621<sup>1)</sup>, which is the screening method for the detection of AOF in solutions using combustion ion chromatograph (CIC). This method involves passing the sample through a granular activated carbon (GAC) column to adsorb AOF onto the activated carbon, followed by combustion to decompose AOF. The resulting gas from AOF is then captured in the adsorbent solution and measured as fluoride ions by ion chromatography. The advantage of CIC is that not only PFAS but also their degradation products and derivatives can be measured as the total amount of organic fluorinated compounds.

In this article, an AOF analysis using a CIC system consisting of an automatic combustion device and ion chromatograph, as well as integrated control software C-IC Solution, is introduced. Not only integrated controlling of combustion device and ion chromatograph, but also AOF analysis in accordance with EPA 1621 can be performed efficiently using C-IC Solution.

#### ■ Instrumentation and analysis

AQF-5000H automatic quick furnace for CIC manufactured by Nittoseiko Analytech and Nexera IC suppression chromatograph for anion analysis manufactured by Shimadzu Corporation were employed as the combustion unit and the ion chromatograph of CIC, respectively (Fig. 1). The sample pretreatment and analytical procedures are as follows.

- (1) The sample passes through TXA-04 absorption unit manufactured by Nittoseiko Analytech, where adsorbable compounds are adsorbed onto GAC.
- (2) Inorganic fluorine compounds are washed out.
- (3) GAC is set in a ceramic boat and combusted.
- (4) Combustion products are collected in adsorbent solution.
- (5) The adsorbent solution is injected into ion chromatograph.

Table 1 shows the analytical conditions for combustion unit and ion chromatograph.

| Table 1 Analytical Conditions    |                                                                               |
|----------------------------------|-------------------------------------------------------------------------------|
| 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 | : 11.1 mL                                                                     |
| System                           | : Nexera IC                                                                   |
| Column                           | : Shim-pack IC-SA2* <sup>1</sup><br>(250 mm × 4.0 mm I.D., 9 μm)              |
| Guard Column                     | : Shim-pack IC-SA2(G)* <sup>2</sup><br>(10 mm × 4.6 mm I.D., 9 μm)            |
| Mobile phase                     | : 1.8 mmol/L Na <sub>2</sub> CO <sub>3</sub><br>1.7 mmol/L NaHCO <sub>3</sub> |
| Flow rate                        | : 1.0 mL/min                                                                  |
| Column temperature               | : 30 °C                                                                       |
| Injection volume                 | : 50 μL                                                                       |
| Suppressor unit                  | : ICDS-Ai                                                                     |
| Detection                        | : Conductivity                                                                |

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In this article, the analytical results are presented following the procedure described in EPA 1621 as follows.

- (1) Creation and evaluation of calibration curve
- (2) Verification of initial performance  
Calculation of retention time window  
Calculations of initial precision and recovery (IPR), method detection limit (MDL), and minimum level (ML)
- (3) Analysis of unknown samples



Fig. 1 Combustion ion chromatograph  
Nexera IC suppressor ion chromatograph for anion analysis manufactured by Shimadzu Corporation (left) and AQF-5000H automatic quick furnace manufactured by Nittoseiko Analytech. (right)

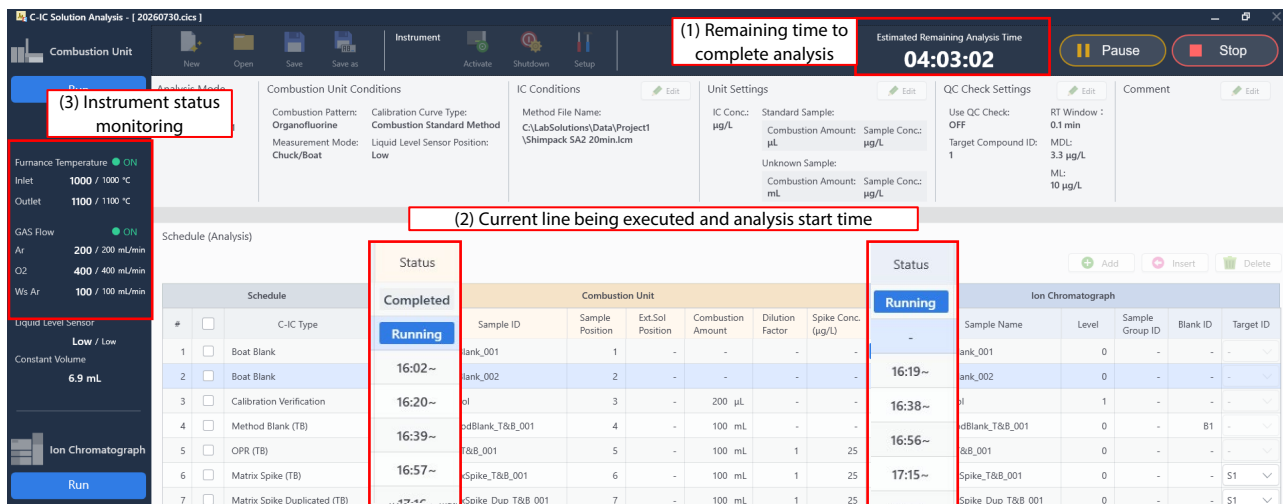


Fig. 2 Analytical control screen of C-IC Solution

### ■ C-IC Solution, integrated control software

C-IC Solution integrated control software enables centralized control of both combustion unit and ion chromatograph. It allows users to: (1) view the total time to complete the analysis; (2) confirm the current run number and the start time of the analysis; and (3) monitor the operational status of both combustion unit and ion chromatograph. Fig. 2 shows the analysis screen of C-IC Solution.

When starting an analysis, simply enter the sample name and the number of calibration levels, and the software automatically creates analytical batch for combustion system and ion chromatograph; it is also possible to create an analytical schedule in accordance with EPA 1621 (Fig. 3).

Figure 3 shows the 'Schedule | Custom Input' window. It includes a dropdown for 'C-IC Type' set to 'Calibration'. Below are input fields for 'Count' (5), 'Sample Name (Prefix)' (STD), 'Sample Position' (1), 'Combustion Amount (μL)' (200), and 'Level' (1).

Fig. 3 Analytical schedule creation window

### ■ Creation and evaluation of calibration curve

EPA 1621 employs the combustion calibration curve method, in which standard solutions are also subjected to combustion pretreatment (without concentration). In this analysis, 200 μL each of sodium fluoride aqueous solutions ranging from 0.1 to 25 mg/L were combusted and adsorbed into 11.1 mL of ultrapure water.

Based on the analysis results of standard solutions, a five-level calibration curve was created. The concentration at each calibration level (fluoride ion concentration in adsorbent solution) was calculated as: prepared concentration × sample combustion volume (0.2 mL) / adsorbent solution volume (11.1 mL). The calibration curve was plotted as a straight line, and it was verified that the recovery rates (%) calculated from the set concentrations and measured concentrations at all calibration levels range within 80–120% specified in EPA 1621. Table 2 shows the set concentration, measured concentration, and recovery rate for each calibration level.

Table 2 Measured concentration and recovery of each calibration level

| Conc. (mg/L) | Calibration levels (μg/L) | Measured Conc. (μg/L) | Recovery(%) |
|--------------|---------------------------|-----------------------|-------------|
| 0.1          | 1.8                       | 1.717                 | 95.4        |
| 0.5          | 9.0                       | 8.926                 | 99.2        |
| 1.0          | 18                        | 17.847                | 99.2        |
| 10.0         | 180                       | 180.503               | 100.3       |
| 25.0         | 450                       | 449.807               | 100.0       |

Using the measured values shown in Table 2, we calculated relative standard error (RSE) according to the following formula. The RSE was 2.7%, which was less than the criterion of 20% specified in EPA 1621.

$$RSE = 100 \times \sqrt{\frac{\sum_{i=1}^n \frac{(x'_i - x_i)^2}{x_i^2}}{n - p}}$$

$x_i$  = Nominal 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)

### ■ Verification of initial performance

Calculation of the Retention Time Window

EPA 1621 requires the establishment of an allowable retention time range (retention time window). This range is set based on the results of three analyses of standard solution for calibration curve. Then average retention time  $\pm$  3-fold of standard deviation is defined as retention time window.

In this article, the retention time window was calculated as  $\pm 0.1$  min based on the results of three analyses of the sodium fluoride standard solution.

IPR

EPA 1621 requires that, as the verification of initial performance, the relative standard deviation (RSD) of measured concentrations from four consecutive analyses of PFHxS standard solution shall be less than 20%, and that the average recovery rate shall be within 80–120%. Both results were verified to be within the specified ranges. Fig. 4 shows the chromatogram of the PFHxS fluoride ion standard solution of 25 μg/L.

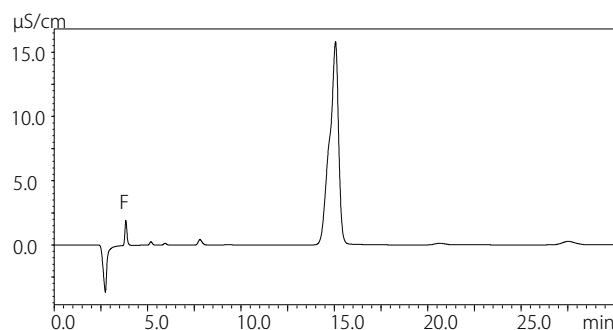


Fig. 4 Chromatogram of PFHxS standard solution

On the C-IC Solution analysis screen (Fig. 5), the fluoride ion concentration (IC concentration) measured by ion chromatograph is automatically converted to the concentration in the sample. Both the IC concentration and the concentration in the sample are simultaneously confirmed on the same screen.

| Retention time (min) | IC Conc | Sample Conc | Corrected Conc | Total Conc | Recovery (%) |
|----------------------|---------|-------------|----------------|------------|--------------|
| 3.821                | 218.206 | 24.221      | -              | 24.221     | 96.9         |

Fig. 5 Data analysis screen of C-IC Solution

The quantitative results (not shown in the table) were calculated by converting them to AOF concentrations (µg/L) in the solution before the activated carbon treatment in accordance with the procedure described in EPA 1621. The conversion formula is shown below, and Table 3 presents the repeatability and recovery rate of AOF concentration (µg/L) from four consecutive analyses of the PFHxS standard solution.

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

AOF = Concentration of adsorbable organic fluorine in µg F-/L

$C_{\text{MB}}$  = Method blank measured concentration (sum of top and bottom GAC) reported without volume corrections

$V_{\text{abs}}$  = Total volume of absorption solution in mL of the sample prior to injection to IC

$V_{\text{MB}}$  = Volume in mL of method blank adsorbed

Table 3 IPR calculation result

|                              | Result | Criterion |
|------------------------------|--------|-----------|
| RSD for AOF concentration(%) | 2.07   | ≤20       |
| Average Recovery (%)         | 94.8   | 80-120    |

#### MDL and ML

To verify the presence of fluoride ions originating from reagents and equipment used in the pretreatment process, 100 mL of ultrapure water was passed through activated carbon and subjected to the same pretreatment as the sample (method blank). Fig. 6 shows the chromatogram of the method blank, and Table 4 presents its quantitative result. The EPA 1621 standard specifies that the quantitative result for the method blank must not exceed 4.0 µg/L, and it was confirmed that the sample met this criterion.

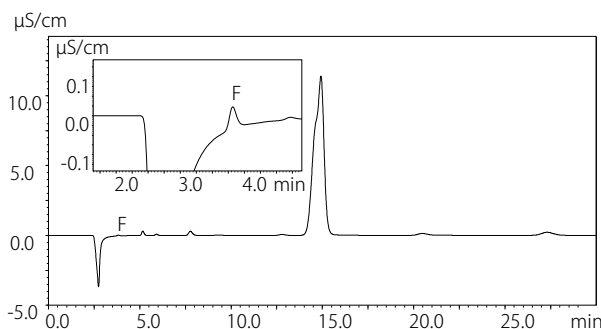


Fig. 6 Chromatogram of method blank

Table 4 Determination result of method blank

|                     | Result | Criterion |
|---------------------|--------|-----------|
| Method Blank (µg/L) | 0.57   | < 4.0     |

In EPA 1621, MDL was calculated in accordance with the description of method procedure and 40 CFR Appendix B to Part 136<sup>2)</sup>. In this method, MDL is defined as the greater of MDL<sup>b</sup>, which is calculated from the result of consecutive analyses of the method blank and MDL<sup>s</sup>, which is calculated from the result of consecutive analyses of 25 µg/L of PFHxS standard solution. The formula used to calculate MDL<sup>b</sup> and MDL<sup>s</sup> is shown below.

$$\text{MDL}^b = X + t_{(n-1, 1-\alpha=0.99)} S^b$$

MDL<sup>b</sup> = the MDL based on method blanks

$X$  = mean of the method blank results

$t_{(n-1, 1-\alpha=0.99)}$  = the Student's t-value appropriate for the single-tailed 99th percentile t statistic and a standard deviation estimate with  $n-1$  degrees of freedom.

$S^b$  = sample standard deviation of the replicate method blank sample analyses.

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

MDL<sup>s</sup> = the method detection limit based on spiked samples

$t_{(n-1, 1-\alpha=0.99)}$  = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with  $n-1$  degrees of freedom.

$S^s$  = sample standard deviation of the replicate spiked sample analyses.

Furthermore, it is stated that the ML calculated using the following equation shall be reported after rounding off to make a form as 1, 2, or  $5 \times 10^n$  (where  $n$  is 0 or integer). In this article, the ML is reported as 5 since the calculation resulted in 3.7. The calculated

results for the MDL and the ML are shown in Table 5.

$$\text{ML} = \text{MDL} \times 3.18$$

Table 5 MDL and ML (µg/L)

| MDL <sup>b</sup> | MDL <sup>s</sup> | MDL  | ML |
|------------------|------------------|------|----|
| 0.74             | 1.16             | 1.16 | 5  |

#### ■ Analysis of unknown sample

The performance of the analytical system for each analytical batch shall be verified when analyzing unknown samples. First, it shall be verified that the recovery rates are within 80–120% and the retention times are within the retention time window calculated in the “verification of initial performance” step (Calibration Verification) through quantitative determination of the calibration standard solution using the calibration curve created in the “Creation and evaluation of calibration curve”. The method blank shall be prepared using the same procedure described above and it shall be verified that the quantified concentration is less than 4.0 µg/L (Method Blank). Furthermore, it shall be verified that the recovery rate for PFHxS standard solution of known concentration is within the range of 70–130% (Ongoing Precision and Recovery, OPR). Furthermore, when analyzing unknown samples, a matrix-spiked sample (Matrix Spike, MS) and its duplicate (Matrix Spike Duplicate, MSD) shall be analyzed to verify that the retention times are within the retention time window and within  $\pm 0.2$  min of the retention time during the verification of initial performance, that the spiked recovery rate is within 50–150%, and that the Relative Percent Difference (RPD) is within 30%. The analytical procedure is shown below.

- (1) Boat Blank Measurement (at least 2)
- (2) Calibration Verification (Low-level)
- (3) Method Blank Measurement
- (4) OPR Measurement
- (5) Samples (10 or fewer)
- (6) Matrix Spike Measurement
- (7) Calibration Verification (Mid-level)
- (8) Samples (10 or fewer)
- (9) Calibration Verification (Mid-level)

C-IC Solution contains QC evaluation function that determines whether the analytical results meet the criteria specified in EPA 1621 or not, enabling support for analyses that are in accordance with testing requirements. Both MS and MSD met the retention time criterion, verifying that the retention time window set during the verification of initial performance was appropriate (Fig. 7).

| IC Conc | Sample Conc | Corrected Conc | Total Conc | Recovery (%) | RSE (%) | RPD (%) | Breakthrough (%) | QC Result | Spike Conc (µg/L) |
|---------|-------------|----------------|------------|--------------|---------|---------|------------------|-----------|-------------------|
| 12.145  | 1.348       | 0.805          | 0.805      | -            | -       | -       | -                | PASS      | -                 |
| 221.818 | 24.622      | 24.079         | 24.079     | 92.6         | -       | -       | -                | PASS      | 25.000            |

RT [RT - CalibCheck RT] ≤ RT Window (0.2 min) : Pass

RT [RT - CalibCheck RT] ≤ RT Window (0.1 min) : Pass

Recovery [50% ≤ Recovery ≤ 150%] : Pass

Fig. 7 QC examination result screen of C-IC Solution

QC evaluation can be performed easily by just entering the values calculated during the verification of initial performance—such as the retention time window—into the settings because the recovery rate and RPD are automatically calculated (Fig.8).

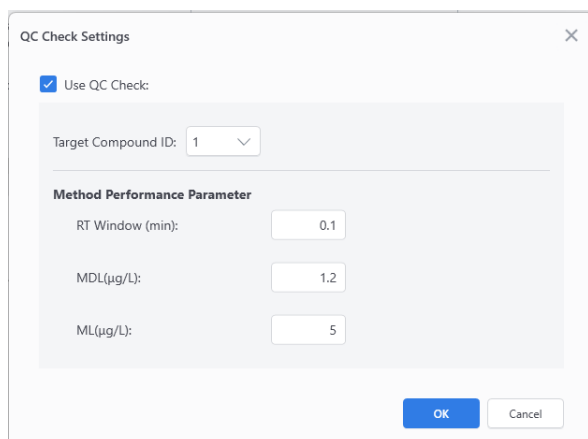


Fig. 8 QC examination setting window of C-IC Solution

Fig. 9-11 show chromatograms of river water, matrix-spiked samples (MS) in which PFHxS standard solution was added to river water to make fluoride ion concentration of 25 µg/L in the sample solution, and sample (MSD) obtained by diluting the MS within the calibration curve range. In this analysis, the dilution factor for the MSD was set to 2.5.

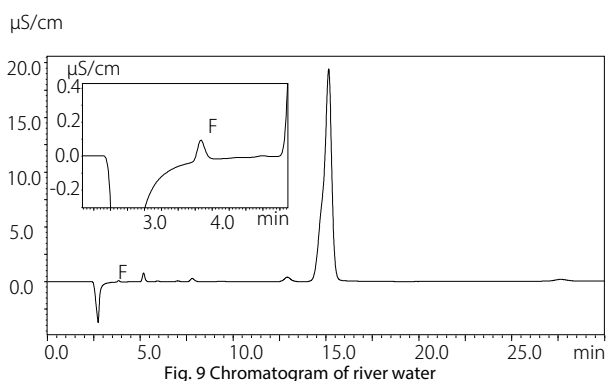


Fig. 9 Chromatogram of river water

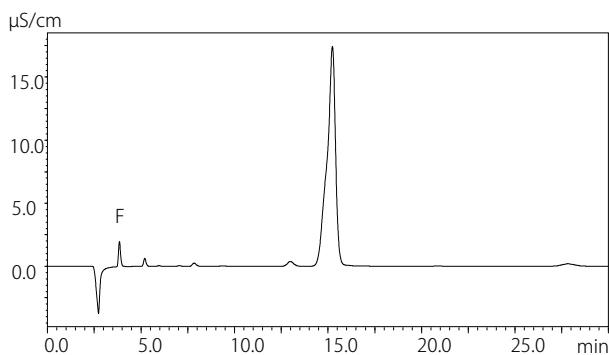


Fig. 10 Chromatogram of MS

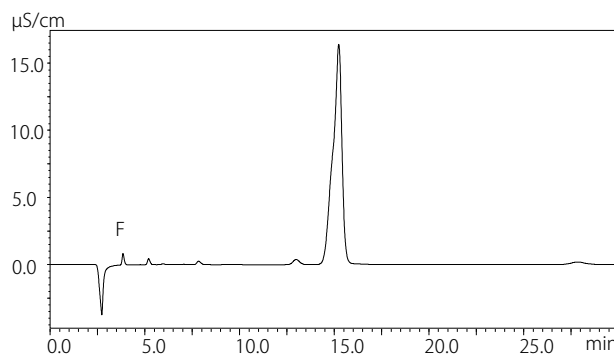


Fig. 11 Chromatogram of MSD (2.5-fold diluted)

EPA 1621 specifies that the spiked recovery and RPD must be calculated based on these analytical results. The determined concentration in MSD was converted to the concentration of the undiluted solution prior to the 2.5-fold dilution, and the RPD was calculated using the following formula. The calculated recovery rate and RPD are shown in Table 6.

$$RPD = \frac{|MS - MSD|}{(MS + MSD)/2} \times 100$$

MS = Percent recovery of the MS

MSD = Percent recovery of the MSD

Table 6 measured concentration, recovery rate, and RPD

|        | Measured Conc.<br>(µg/L) | Recovery(%) | RPD *1 |
|--------|--------------------------|-------------|--------|
| Sample | 0.925                    | --          | --     |
| MS     | 24.1                     | 92.6        | --     |
| MSD    | 25.6                     | 98.7        | 6.3    |

\*1:RPD was calculated using the recovery rates before rounding off

## Conclusion

In this article, AOF was successfully determined in accordance with EPA 1621 using C-IC system consisting of AQF-5000H automatic combustion unit Nittoseiko Analytech and the Nexera IC ion chromatograph from Shimadzu. The system demonstrated excellent precision and recovery performance in the IPR test, confirming its suitability for reliable AOF screening.

Beyond analytical performance, the combination of the AQF-5000H, Nexera IC, and C-IC Solution provides a streamlined workflow from combustion and IC analysis to data processing and quality control evaluation. Through a single software platform, users can centrally control the entire CIC system, automate EPA 1621-compliant analytical sequences, and simplify QC assessment. This integrated workflow helps improve laboratory efficiency, reduce manual operations, and support consistent, reliable AOF analysis.

## References

- 1) EPA 1621 Screening Method for the Determination of AOF in Aqueous Matrices by CIC
- 2) 40 CFR Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 2

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