



Challenge

A simple, fast, and sensitive detection of total fluorine in wastewater.

Solution

With regard to the determination of a sum parameter of fluorinated compounds, a species-unspecific response of high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS) was developed.

A Novel Method for the Fast, Sensitive, and Simple Analysis of Total Fluorine in Wastewater

Introduction

The introduction of carbon-fluorine bonds into organic compounds is known to profoundly influence their chemical and physical properties when compared to their non-fluorinated analogues¹. Many of the most important products of the chemical and life-science industries, from pharmaceuticals, through fine and specialty chemicals, to polymers, rely on organic fluorine chemistry for their useful properties. The accelerating production volumes of fluorinated organic substances expectably leads to their increasing release into the environment. Some of these substances are already listed as persistent organic pollutants by the Stockholm Convention (Annex B -restriction) and the European water framework directive (WFD).

Per- and polyfluoroalkyl substances (PFAS) are a large class of synthetic chemicals that present numerous analytical challenges, including their widespread presence in a variety of environmental samples². In the US, PFAS may contaminate public drinking-water systems that serve an estimated 19 million people³. The United States Environmental Protection Agency (EPA) is continuing to aggressively implement their PFAS Action Plan – the most comprehensive cross-agency plan ever to address an emerging chemical of concern². The EPA has established a non-enforceable health advisory level of 70 parts per trillion (ppt) for the sum of pentadecafluorooctanoic acid (PFOA) and heptadecafluorooctanesulfonic acid (PFOS) for drinking water. The EPA is developing a potential rapid screening tool to identify total PFAS presence and absence in 2021. This eventual standard operating procedure will be used to quantify Total Organic Fluorine (TOF)⁴.

Therefore, a sensitive, fast, and simple TOF detection method is needed for environment pollution monitoring and control. The method is based on a combination of solid-phase extraction (SPE) with high-resolution-continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS). In another Application Note, "Determination of Extractable Organically Bound Fluorine (EOF) in Surface Water", the solid phase extraction (SPE) procedure has been fully discussed for the extraction of fluorinated compounds. HR-CS GF MAS was used to detect total fluorine via in-situ formation of gallium(I) fluoride (GaF) molecules. In this study, we focus on improving the performance of Total Fluorine (TF) analysis in wastewater by optimizing HR-CS GF MAS method and applying novel calibration strategies.

Method Development Strategy

For the quantification of fluorinated organic compounds as a sum parameter, a species-unspecific response for HR-CS GF MAS method needs to be developed and optimized. From our past research, gallium has proven to enable the most sensitive fluorine detection via diatomic GaF formation. The characteristic molecular absorption of the GaF is then detected by HR-CS GF MAS. To achieve the best signal, the furnace tube was conditioned with the molecule forming agent (Ga) and modifiers (Pd/Mg/Zr/Ba) before the sample was injected. From the literature, it's known that melting point/vapor pressure of the fluorinated compounds significantly impacts the recovery rates of the different compounds. Thus, the drying and pyrolysis procedure in the furnace program were optimized to keep possible losses of fluorinated compounds as low as possible. To evaluate the optimization approach, 24 different fluorine compounds were mixed for the QC sample. These 24 compounds were selected with different numbers of fluorine atoms and boiling points. Calibration strategies were developed to obtain the best recovery rate for this QC sample.

Materials and Methods

Reagents:

- Ultrapure grade HNO₃
- 0.05% TritonX-100
- Pd/Mg/Zr modifier (1 g/L Pd, 0.5 g/L Mg, 0.02 g/L Zr)
- Ba modifier (10 mg/L)
- Ga solution (10 g/L)
- Zr stock solution (1 g/L)
- Certificated F stock solution (0.1 g/L F ICP standard as NaF)
- Heptadecafluorooctanesulfonic acid solution (PFOS, 100 µg/mL in methanol, analytical standard)
- Pentadecafluorooctanoic acid solution (PFOA, 100 µg/mL in methanol, analytical standard)

Samples:

- QC sample: 24 fluorinated organic compounds mixture (TOF about 128 µg/L)
- Wastewater sample

Instrumentation

The contrAA® 800 G graphite furnace AAS with AS-GF autosampler controlled by ASpect CS software was used for the determination of fluorine. Before use, the graphite tube was first coated with zirconium (35 µL stock solution, 6 times). The fluorine content was determined by measuring the intensity of the gallium monofluoride absorption band. During the analysis, fluorine is converted stoichiometrically to GaF in the presence of gallium. To improve the sensitivity, a conditioning procedure was included in the furnace program. Each sample was analyzed with three replicates. Table 2 and Table 3 show the method settings and furnace program.

Table 1: Instrument specifications

| Parameter | Specification |
|-------------------|---|
| Instrument | contrAA 800 G |
| Furnace tube type | PIN platform |
| Autosampler | AS-GF |
| Injected volume | 4-20 µL (standards), 20 µL (sample) |
| Rinsing solution | 2% HNO ₃ , 0.05% TritonX-100 |

Table 2: Method settings and evaluation parameters

| Molecule | Wave-length [nm] | No. of eval. pixels | T Pyr. [°C] | T Atomis. [°C] | Ramp [°C/s] | Meas. Time [s] | Modifier | Baseline correction |
|----------|------------------|---------------------|-------------|----------------|-------------|----------------|--|---------------------|
| GaF | 211.248 | 5 | 500 | 1450 | 1200 | 5 | 5 µL Pd/Mg/Zr modifier* 5 µL Ga solution* 3 µL Ga solution 5 µL Ba solution | IBC |

Note: *-use in the conditioning step

Table 3: Furnace program for detection of GaF molecule

| Step | Name | Temp (°C) | Ramp (°C/s) | Hold (s) | Gas purge |
|------|--------------|-----------|-------------|----------|-----------|
| 1 | Drying* | 80 | 6 | 5 | max |
| 2 | Drying | 100 | 6 | 5 | max |
| 3 | Drying | 160 | 10 | 5 | max |
| 4 | Drying | 350 | 25 | 10 | max |
| 5 | Drying | 1100 | 500 | 12 | max |
| 6 | Drying | 70 | NP | 10 | max |
| 7 | Drying^ | 80 | 2 | 10 | max |
| 8 | Drying | 110 | 5 | 15 | max |
| 9 | Pyrolysis | 250 | 50 | 5 | max |
| 10 | Pyrolysis | 500 | 200 | 5 | max |
| 11 | Gas adaption | 500 | 0 | 5 | stop |
| 12 | Atomization | 1450 | 1200 | 5 | stop |
| 13 | Clean | 2450 | 1200 | 4 | max |

Note: *-modifier injection for pretreatment, ^-sample injection

Calibration Strategy

From the past research and literature, the melting point/vapor pressure of the fluorinated compounds plays an important role for total fluorine analysis. If the vapor pressure at a given temperature of the respective substance is high, the analyte is transferred into the gas phase and carried away by the argon stream during the furnace program before detection. Thus, the calibration standards should be selected to have similar behavior to the samples. To find the best calibration strategy for the waste water, three different calibration sets were prepared. Table 4 shows the components of each calibration set.

For the inorganic fluoride calibration (inorganic F), a 1000 ppm NaF stock solution was used for preparing calibration standards. Three common fluorinated compounds, PFOS, PFOA and HFPO-DA, were selected to prepare organic fluorine (organic F) standards. The inorganic and organic mixture standard was also prepared with NaF, PFOS, PFOA and HFPO-DA. Table 5 shows the concentrations and absorbances of the standards, as well as the linearity of calibration. Based on the calibration curve and measured blank values, the lowest LOD of 4.00 µg/L was achieved with the inorganic and organic mixture calibration. In Table 5, the inorganic fluoride calibration standards show the highest signal while the organic calibration standards show the lowest. The different signal responses of organic and inorganic substances depends on their thermal stability. Volatile PFAS are partially lost during the drying and pyrolysis steps of the furnace program. However, inorganic fluoride is thermally stable during these steps. In Table 6, the clear and interference-free GaF absorbance spectra (blue) at 211.248 nm is shown from the three calibration sets.

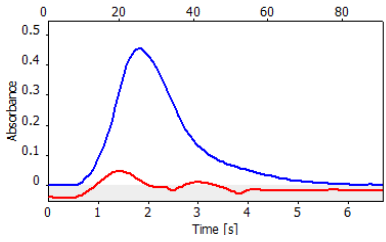
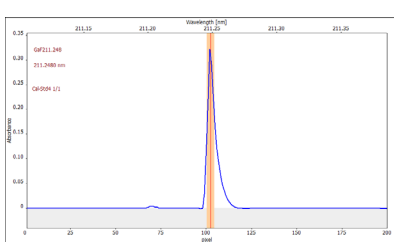
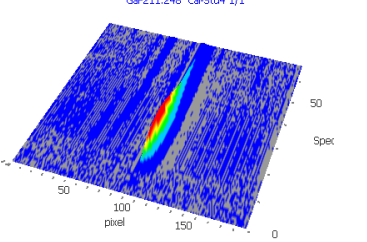
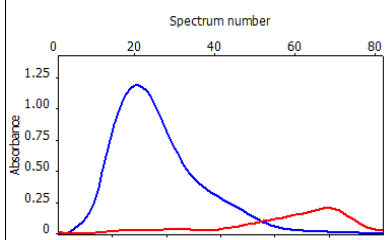
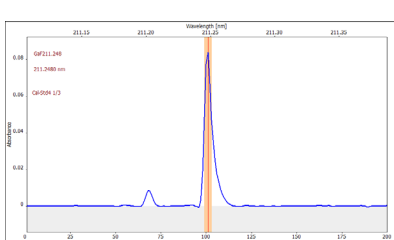
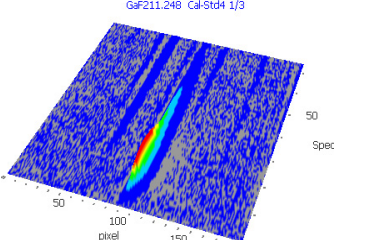
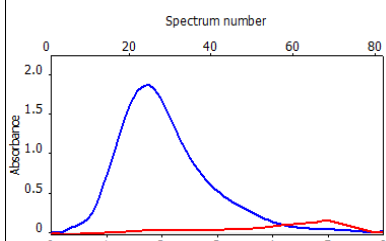
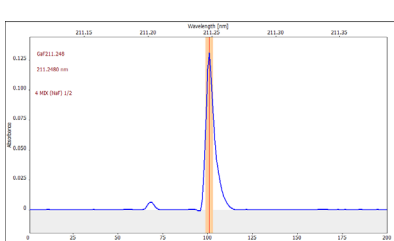
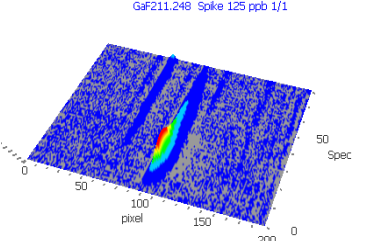
Table 4: Concentration sets

| Calibration Set | F Compounds | Ratio |
|---------------------------------|--------------------------|---------|
| Inorganic F | NaF | |
| Organic F | PFOS, PFOA, HFPO-DA | 1:1:1 |
| Inorganic and organic F mixture | NaF, PFOS, PFOA, HFPO-DA | 1:1:1:1 |

Table 5: Type and quality of calibration

| Name | Conc. | Inorganic F | Organic F | Inorganic and organic mixture |
|----------------|-------|-------------|-----------|-------------------------------|
| Unit | µg/L | Abs | Abs | Abs |
| Cal-Zero1 | 0 | 0.1726 | 0.1153 | 0.1709 |
| Cal-Std1 | 125 | 1.6650 | 0.5177 | 1.1601 |
| Cal-Std2 | 250 | 3.0402 | 1.0367 | 1.7833 |
| Cal-Std3 | 375 | 4.4542 | 1.4847 | 2.4628 |
| Cal-Std4 | 500 | 5.9955 | 1.9403 | 3.0694 |
| R ² | | 0.9993 | 0.9999 | 0.9808 |
| LOD (µg/L) | | 7.74 | 12.58 | 4.00 |

Table 6: Characteristic signal shape and spectral vicinity of the analyte line

| Element | Signal profile* | Spectral vicinity | 3D spectrum |
|---|--|---|--|
| Inorganic F Cal 4 |  |  |  |
| Organic F Cal 4 |  |  |  |
| Inorganic and organic mixture Cal 4 |  |  |  |

*blue: GaF analyte signal, red: background signal

Results and Discussion

1. Result of Inorganic F Calibration Strategy

With the inorganic F calibration strategy, the QC standard of 24 fluorinated organic compounds shows a 38% recovery rate (Table 7). Differences in signal response result in the low recovery rate for PFAS when using NaF solutions as the calibration standard. When the QC sample is spiked with 100 µg/L F (as NaF), it shows a good spike recovery rate of 114%.

Table 7: Measurement results by inorganic F calibration

| Samples | Conc. (µg/L) | Recovery (%) |
|--------------------------------------|--------------|--------------|
| Blank water | <LOQ | |
| QC sample | 48.9 | 38 |
| QC sample spiked with 100 µg/L (NaF) | 162.5 | 114 |
| Wastewater | 348.2 | |

2. Result of Organic F Calibration Strategy

With the organic F calibration strategy, the QC sample's recovery is 190%. This overestimation of PFAS is due to the different thermal stabilities of the various organic fluorinated compounds. When the QC is spiked with 100 µg/L NaF, a 275% spike recovery rate is obtained due to the stronger stability and signal response of NaF. Both the QC and wastewater samples were spiked with 125 µg/L F from the TOF mixture. This TOF mixture is composed of the same compounds as the organic calibration standards. The spike recovery rates for both the QC and wastewater are 74%.

Table 8: Measurement results by organic F calibration

| Samples | Conc. (µg/L) | Recovery (%) |
|--|--------------|--------------|
| Blank water | <LOQ | |
| QC sample | 224.7 | 174 |
| QC sample spiked with 125 µg/L F (TOF*) | 316.7 | 74 |
| QC sample spiked with 100 µg/L F (NaF) | 628.1 | 275 |
| Wastewater | 4882.5 | |
| Wastewater (1:50 dilution) spiked with 125 µg/L F (TOF*) | | 74 |

*TOF = PFOS, PFOA, HFPO-DA (ratio 1:1:1)

3. Result of Inorganic and Organic Mixture Calibration Strategy

From Table 9, the organic and inorganic F mixture calibration strategy provides the best approximation of sample analyte characteristics. The QC samples recovery rate is 100%. The QC sample and wastewater sample were spiked with 125 µg/L F from the TF mixture. The compounds in the TF mixture are the same as the inorganic and organic mixture calibration standards. The spike recovery rates are 85% and 86% for the QC sample and wastewater sample, respectively. The QC is also spiked with inorganic F and the recovery rate is overestimated as 167%. This is also due to the higher thermal stability of inorganic NaF. Comparison between the three calibration strategies demonstrates the dramatic influence the calibration components can impact the analysis results. For this specific QC sample, the inorganic and organic F mixture calibration strategy is the optimal choice.

Table 9: Measurement results by inorganic and organic mixture calibration

| Samples | Conc. (µg/L) | Recovery (%) |
|---|--------------|--------------|
| Blank water | <LOQ | |
| QC sample | 127.6 | 100 |
| QC sample spike with 125 µg/L F (TF*) | 252.6 | 85 |
| QC standard spike with 100 µg/L F (NaF) | 380.9 | 167 |
| Wastewater | 1936.5 | |
| Wastewater (1:50) spike with 125 µg/L F (TF*) | | 86 |

*TF = NaF, PFOS, PFOA, HFPO-DA (ratio 1:1:1:1)

4. Long-term stability test

To evaluate the long-term stability of this method, the QC sample was tested on three separate days each one week apart. The three tests all used Test 1's calibration curve without recalibration. In this period, the RSD is 5.7% of those three tests (Table 10). This demonstrates the excellent long-term stability of the method.

Table 10: Long-term stability test

| | Conc. (µg/L) | RSD (5 Replicates) |
|-----------------|--------------|--------------------|
| Test 1 (week 1) | 127.6 | 3.8 % |
| Test 2 (week 2) | 113.8 | 3.0% |
| Test 3 (week 3) | 120.2 | 2.7% |
| Average Conc. | 120.5 | |
| RSD | 5.7% | |

5. Blank value

During method optimization, relatively high blank values were observed. The carry-over effect in the sample introduction system was considered to be the largest contributing factor. By adding HNO₃ and TritonX-100 in the rinsing solution, the blank value was lower. It's very important to use F-free modifiers. Using high purity salt, such as Gallium (III) nitrate hydrate, to prepare modifiers is recommended.

Conclusion

In this study, a fast, easy, and sensitive complementary method for total fluorine analysis in wastewater is presented. This study shows that the MAS method can be successfully applied using the contraAA 800 G for the measurements. The optimized furnace program and calibration strategy provide high sample throughput, sensitivity, and accuracy. Only 3.5 minutes/replicate is needed for each sample. 100% recovery rate of QC sample is successfully achieved with an inorganic and organic mixture calibration strategy. The lowest LOD of 4 ppb is also achieved the inorganic and organic mixture calibration strategy. The results of fluorine determination by HR-CS-GF MAS show good reproducibility and long-term stability. Sample dilution and spiking can be easily achieved with an AS-GF autosampler. No additional cleaning steps are required for this method.

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