# Memo

BTO 2024.205(s)

| From | Subject | Date |
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| Elvio Amato | Risico's van PFAS voor drinkwaterbedrijven | 19 December 2023 |
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| Waternet, Vitens | | 1/4 |

## 1.1 Introduction

Per- and polyfluorinated compounds (PFAS) are a broad group of anthropogenic organic substances that have been widely used in numerous industrial processes since the 1940s. Due to their persistence, bioaccumulation and toxicity, PFAS have been increasingly studied worldwide. Current monitoring programs include the analysis of PFAS, but only a limited number of compounds are investigated. Increasing research and regulatory attention is now focused on the assessment of a larger and more comprehensive group of PFAS.

In the recent project (Amato et al., 2023b), KWR developed advanced analytical techniques to identify a wide range of PFAS in surface, ground and drinking water using high-resolution mass spectrometry (HRMS), and suspect and non-target screening methods (NTS). In addition, a procedure to estimate total oxidizable precursors (TOP) has been validated at KWR. However, more approaches exist that measure the total amount of organically bound fluorine as a proxy of total PFAS concentrations, including adsorbable organic fluorine (AOF) methods. Although non-specific (i.e., it can only measure total fluorine content, but not specific compounds), this method can be useful for rapid preliminary screening, and is currently considered by the European Commission for implementation in the Drinking Water Directive as a method to determine total fluorine in water (Proposal for a Directive of the European Parliament and of the Council on the Quality of Water Intended for Human Consumption, 2020). Thus, the application and integration of these methods with the existing ones is also particularly relevant from a legislative point of view

However, AOF has only been used to a limited extent in the Netherlands for applications in water monitoring, and is currently not sufficiently sensitive for screening of drinking water samples (i.e., detection limits of approximately 1 µg/L are typically reported). Thus, in this project we focused on a method based on particle induced gamma ray emission (PIGE) spectroscopy. This method has been recently applied to water measurements and is expected to more closely match the sensitivity required to determine total organic fluorine in drinking water samples (Tighe et al., 2021).

The purpose of this project is to support and complement the ongoing BTO research aiming to achieve a comprehensive assessment of PFAS contamination in the (drinking) water.

## 1.2 Methods

Samples consisted of (i) drinking water (KWR), (ii) surface water (Lekkanaal), (iii), seawater (North Sea), and (iv) ultrapure water spiked with a standard mixture (Table 1). All samples were prepared in plastic containers (3.5 L). The fortified sample was prepared by adding 1.3 mL of standard mixture to 3.5 L of ultrapure water, whereas the remaining samples were obtained by transferring 3.5 L into the plastic containers. The seawater sample was obtained by mixing samples collected in a previous study (Amato et al., 2023a). The analytical procedure used was adapted from Tighe et al. (2021), and involved extraction of fluorine by gravity filtration of the sample through an activated carbon felt, followed by analysis of total fluorine using particle induced gamma ray emission (PIGE) spectroscopy.

This technique uses a proton beam directed onto the filter containing PFAS molecules. Fluorine nuclei from PFAS molecules are excited in this process, and during de-excitation, the fluorine nuclei emit gamma-rays that are measured by a detector. The obtained spectrum includes a fluorine peak from which the fluorine concentration can be determined. After analysis, the carbon felt was washed with $HNO_3$ to remove potential inorganic fluorine interferences, and analysed again to provide a measure of total organic fluorine. However, this procedure is expected to results in the removal of short-chain PFAS ($C < 4$) as well. PIGE measurements were expressed as parts per trillion (ppt), and the limit of quantification (LOD) of this technique was approximately 25 ppt (Tighe et al., 2021).

Table 1. Concentrations of the PFAS included in the standard mixture solution.

| | Concentration (mg/L) |
|---|---|
| PFBA | 0.25 |
| PFHxA | 0.25 |
| PFHpA | 0.25 |
| PFOA | 0.26 |
| PFNA | 0.25 |
| PFDA | 0.26 |
| PFUnDA | 0.25 |
| PFDoDA | 0.26 |
| PFTrDA | 0.26 |
| PFBS | 0.25 |
| PFPS/PFPeS | 0.24 |
| PFHxS | 0.25 |
| PFHpS | 0.24 |
| PFOS | 0.25 |
| PFDS | 0.24 |

### 1.3 Results and discussion

Total organic F concentrations ranged between < 25 and 1252 ± 97 ppt, which were measured in drinking water and seawater, respectively (Table 2). The LOQ of this technique is approximately 25 ppt (i.e., 25 ng/L of F), which, expressed as PFOA concentration, corresponds to approximately 36 ng/L. This is lower than the LOQs typically reported for AOF (i.e., ~ 1 µg/L of F), and higher than those reported for TOP assay (i.e., 0.1 - 1 ng/L). These results indicate that the technique is not suitable to accurately measure total fluorine in drinking water, however, it is still useful for screening PFAS at contamination levels that are relevant for drinking water.

The total organic fluorine concentration measured by PIGE in a sample spiked with known amounts of PFAS (664 ppt) was similar to theoretical concentration expected to be found in the sample (919 ppt). Fluorine concentrations in the surface water, seawater, and spiked water samples, expressed as PFOA concentrations, were 284, 1815, and 962 ng/L, respectively. Levels in the surface water sample were overall consistent with expected values, whereas seawater concentrations appeared unexpectedly high. After washing the carbon felt with $HNO_3$, concentrations slightly increased for all samples, except for the seawater sample. While the wash is performed to remove fluoride interferences, and thus lower fluorine concentrations should be expected, increasing concentrations after acidification were attributed to removal of organic matter, which has been shown to contribute to signal suppression.

In the seawater sample, fluorine concentrations decreased after wash with $HNO_3$. This was attributed to removal of fluoride interferences, as fluoride is not expected to bind to the carbon felt at $pH < 2$. Fluorine concentrations before wash were in the low ppb range (i.e., 1252 ng/L), which is much lower than the levels typically reported in seawater (i.e., low ppm range (mg/L)) (Bewers, 1971; Miyake et al., 2007). This suggests that the carbon felt adsorbed a very small fraction of the total fluoride present in the sample, which was potentially removed after wash with $HNO_3$.

PFAS concentrations in the seawater sample ranged from < 0.5 to 3 ng/L, except for PFOS which was found at 12 ng/L (Amato et al., 2023a). These concentrations are much lower than those measured by PIGE, suggesting that a considerable fraction of PFAS that is not accounted for using conventional targeted analysis may potentially be present in the sample. The fluorine concentration measured in the spiked sample after acidification (796 ppt) was consistent with the theoretical concentration (919 ppt). This indicated that PIGE may be a suitable technique for measuring total organic fluorine and screening PFAS in water samples.

Table 2. Fluorine concentrations measured using PIGE before and after acidification of water samples.

| | Before acidification | | After acidification | |
|---|---|---|---|---|
| Sample | F concentration (ppt) | Error (ppt) | F concentration (ppt) | Error (ppt) |
| Tap water | 0 | 16 | 66 | 17 |
| Surface water | 196 | 22 | 242 | 22 |
| Seawater | 1252 | 97 | 982 | 82 |
| Spiked sample | 664 | 37 | 796 | 39 |

## 1.4 Conclusions

Results suggest that PIGE is a promising technique for screening of total organic fluorine in water samples. Good agreement between theoretical and measured fluorine concentrations in a spiked sample containing known amounts of PFAS indicated that the technique is suitable for the assessment of total PFAS. However, the spiked sample did not contain ultrashort-chain PFAS ($C < 4$) – such as trifluoroacetic acid (TFA) – which typically occur at very high levels in water samples. Thus, it is unclear how PIGE would perform in the presence of these compounds, especially considering potential challenges in the sample preparation (i.e., interferences of organic carbon, and affinity of the carbon felt for ultrashort-chain PFAS). Future studies should focus on the direct and more comprehensive comparison between targeted analysis (including ultrashort-chain PFAS), PIGE, and other methods such as total oxidizable precursors (TOP) assay, using spiked samples as well as different types of water.

## References

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