SCREENING TECHNIQUE FOR ADSORBABLE ORGANIC FLUORIDE (AOF) CONCENTRATIONS WITH THE XPREP C-IC

The analyses of polyfluoroalkyl substances (PFAS) is a well-discussed topic in today's environmental market. Measurements of PFAS concentrations are a requirement to get a better insight in the effect of PFAS components on the environment and health.

Traditional PFAS analytical methods are focused on the speciation of all the PFAS components with separation techniques. Currently, thousands of PFAS components have been produced and identified, which makes the analyses for these speciated components more and more complex. For this reason, the market for PFAS analysis is requesting a simple and reliable fast screening technique, which can determine the total amount of PFAS components in aqueous matrices. This requirement set things in motion to develop a new method for analyses for AOF.

The determination of AOF is based on the same principle as AOX analyses: A technique already used for decades in environmental laboratories for monitoring the amount of organic halides (Chlorine/Bromine/Iodine) in water. With AOX analysis, coulometry is used as the traditional quantification and detection technique, for the analyses of AOF the quantification and detection is done by an Ion Chromatograph (IC).

Currently, the DIN and ASTM working groups are developing methods for the analyses of AOF, aiming at measuring ranges of 1 to 100 µg/L AOF. The methods used for sample preparation are quite straightforward and are easy to learn for operators.

Instrumentation:

The Xprep C-IC consists of 2 parts: A combustion unit and the fraction collection unit. In the combustion unit, the sample is introduced and combusted. In the fraction collection unit, the combustion gasses are conditioned and collected in individual collection vials. The fraction collection unit is equipped with a sample tray for 65 positions. The main advantages of collecting the sample fractions in separate vials on the sample tray compared to a single absorption tube are:

- The fraction collection unit can also be used as an autosampler for normal IC analyses.
- Combusted samples are stored after the IC analyses, they can be reanalyzed at any later time.
- Additionally any IC (or other analytical instrument) can be coupled to the fraction collector for direct online analysis after combustion.
- No memory or carryover effects caused by the previous sample

The Xprep-C-IC system can work fully automated day and night, for combustion collection and injection of the samples in any IC system.

Sample treatment:

An adequate amount of sample must be taken in account to reach the lower end of the detection limits. Normal AOX analyses requires the sample to have a pH of 2 or lower, for AOF analyses the sample must have a neutral pH. This neutral pH is essential as inorganic fluoride present in the sample will adsorb irreversible onto the activated carbon if the pH is 2 or lower. The irreversible adsorption will result in a positive bias for samples containing inorganic fluoride.

The test-sample then can be treated according to two general accepted methods, the "Batch" or "Column" method.

The batch method principle consists of a sample that is shaken with an amount of activated carbon for 1 hour. During the shaking, all the PFAS components will be adsorbed onto the activated carbon. After 1 hour of shaking the sample, the total liquid with activated carbon is filtrated over a reusable quartz filter. The retained carbon on the quartz filter (containing the adsorbed PFAS components) is then rinsed with an amount of pH-neutral nitrate wash solution: This is done to ensure no inorganic fluoride components stay adsorbed on the activated carbon.

For the column method, the sample is eluted with a constant speed over 2 columns, which are set in series of each other. AOF components will be adsorbed onto the activated carbon column during the elution (a technique comparable with standard SPE methods). The first column, should adsorb the majority of the PFAS components. The second column is used as a security column in case the first column reaches its retaining capacity. When all the sample is eluted over the 2 columns, the columns will be rinsed with a pH neutral nitrate solution to remove any adsorbed inorganic fluoride components.

Besides the Xprep C-IC, Trace Elemental Instruments has more devices available in the portfolio for different types of required sample pretreatment for AOF analyses. Special instrumentation can be used to aid and automate both ways of sample treatment.
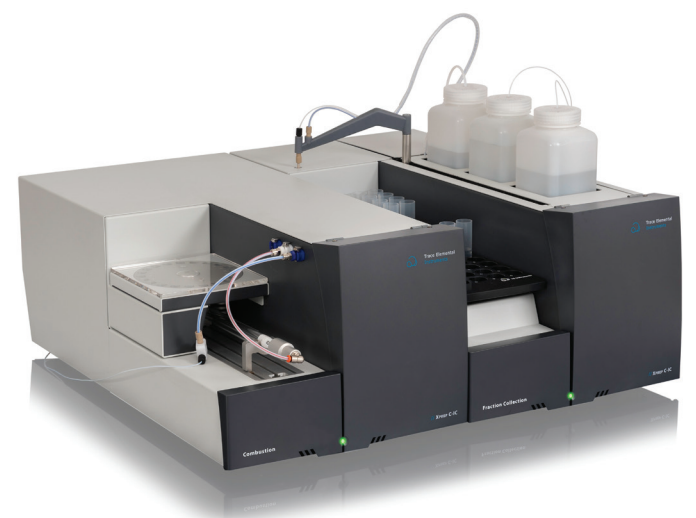
Combustion:

Once the sample pretreatment is finished, the activated carbon samples have to be combusted to free all Fluoride by pyrohydrolitic combustion: A controlled combustion under high humidity conditions in an oxygen-rich environment at high temperatures (minimum 950°C). The high humidity prevents the formed Hydrogen Fluoride to interact with the surfaces of the combustion tube.

Sample introduction can be automated with an autosampler for the AOF batch method, as well as with a sampler for the AOF column method.

At the furnace exit, the gases are cooled down to ambient temperature and guided into a collection vial with an absorption solution. The collection vial now contains the component of interest in the form of hydrogen fluoride.

During the combustion of activated carbon, a significant amount of ashes is formed. These ashes are not allowed to leave the furnace tube to prevent possible blockages inside the instrumentation or damage to the analytical IC columns. To avoid

Xprep C-IC equipped with the solids autosampler for the AOF method

this from happening, a special filter is positioned at the back of the furnace tube to catch all the formed ashes. When the sample is fully combusted in the furnace, the introduction mechanism will return to the home position to cooldown for the introduction of the next sample.

Analysis:

At this point, the sample is ready for the IC analyses. This can be performed in 2 ways:

- Online: The Xprep collector system is directly connected to an IC
- Offline: IC (or other analysis system) is located at a different location in the laboratory

Online:

When the Xprep C-IC is connected to an IC, the Xprep C-IC will automatically fill the sample loop of the IC. When the sample loop is fully filled with sample, the Xprep C-IC will send a signal towards the IC to start the measurement. The IC will inject the sample loop on the analytical column, and the IC measurement starts. Parallel to the IC analysis the next sample can already be introduced and collected in a separated vial.

Offline:

The Xprep C-IC handles all the combustion steps and collections steps stand-alone without any additional analytical instrument (e.g. IC). The setup will only be used as a combustion and collection system. Samples can be manually transferred to any analytical instrument for future analysis.
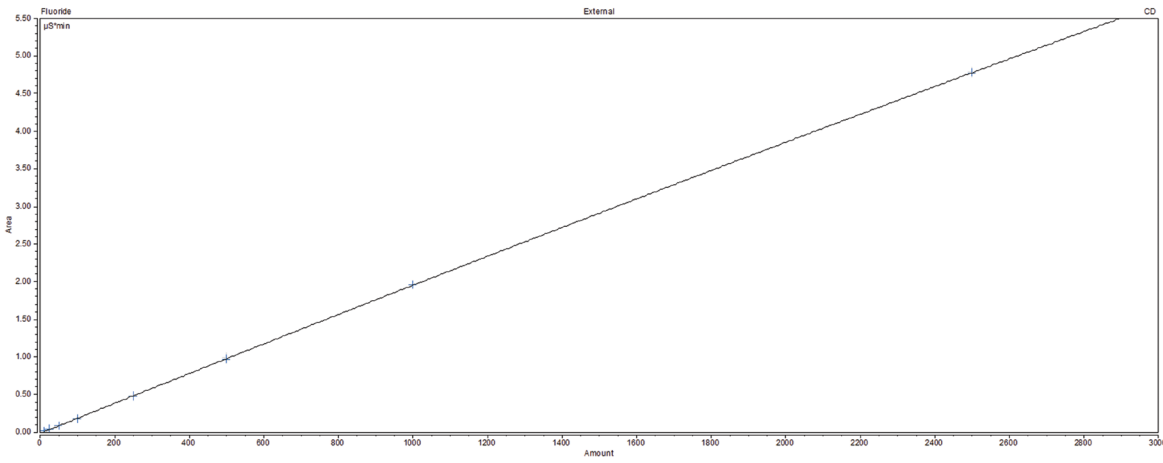
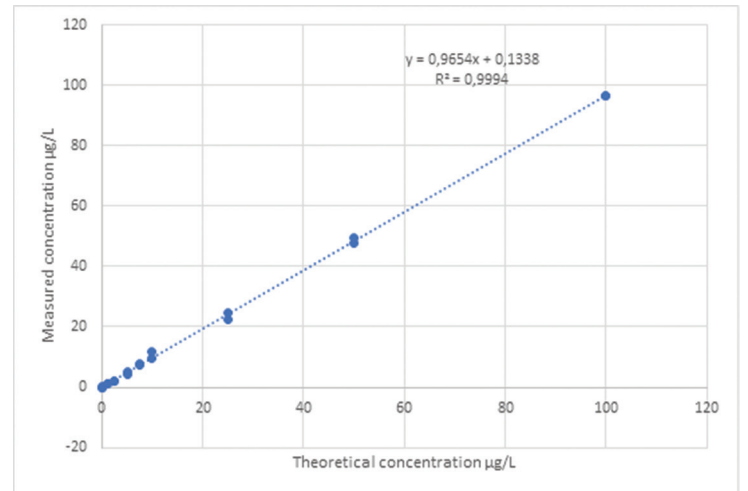Figure 1: Calibration line from the IC from 10 µg/L up to 2500 µg/L. Linearity: R2=0.9998, RSD% = 0.776

Figure 2: Graph showing the fit of the initial check.

Calibration:

According to the draft methods of the ASTM and DIN, the calibration is done through a direct calibration of the IC with inorganic fluoride standards.

Sample Calculation and Results:

After the samples are measured, results will be corrected for sample amount and the volume used in the collection vial, followed by blank value subtraction.

The following formula is used for the correction of the calculation of the results:

$$C_{AOF} = \left(C_{sample} \times \frac{V_{cvs}}{V_s} - C_{blank} \times \frac{V_{cvs}}{V_s}\right) \times D$$

C_{AOF} = concentration AOF in the sample (µg/L)

C_{sample} = measured fluoride concentration in the sample (µg/L)

C_{blank} = measured fluoride concentration in the blank sample (µg/L)

V_{CVS} = volume in the collection vial of the sample (mL)

V_{Cvb} = volume in the collection vial for the blank sample (mL)

V_s = volume of the test sample (mL)

V_b = volume of the blank test sample (mL)

D = Dilution factor of the sample

THEORETICAL CONCENTRATION (µG/L)	MEASUREMENT 1 (µG/L)	MEASUREMENT 2 (µG/L)	MEASUREMENT 3 (µG/L)
0	0.18	-0.17	-0.011
1.0	1.1	1.3	
2.5	2.1	2.0	
5.0	4.9	4.3	
7.5	7.9	7.5	
10	12	10	
25	23	25	
50	50	48	
100	97	96	

Table 1: Results of the initial check

For validation of the AOF analyses on the CIC setup, an initial check has to be performed. This initial check must contain at least 3 blank samples and a minimum of 5 check standards (covering the complete measuring range). The theoretical concentrations then must be plotted against their measured concentration following a forced linear trendline through the data points.

For this linear trendline the correlation coefficient (r2) must be better than 0.99, and the slope of the trendline must be between 0.9 and 1.1. The results below show the excellent performance of the Xprep C-IC over the entire working range for the AOF analyses.

These results show that the Xprep C-IC passes the criteria of the initial check for the AOF analyses with flying colors.

Contact TE Instruments for more information about this innovative solution, such as the related application data!
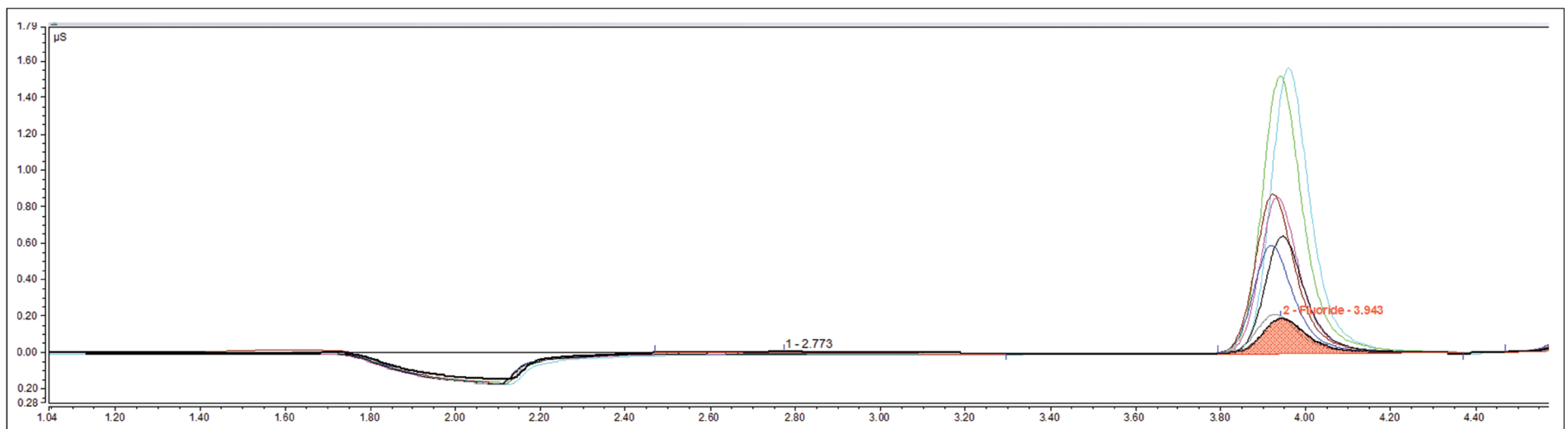

Figure 3: Zoomed in overlay of the fluoride peaks, containing 0/1/2.5/ 5 µg/L RT=3.8 minutes.

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