



SPECIATED AOX ANALYSIS BY COMBUSTION IC

Adsorbable Organic Fluoride, Chloride, and Bromide in Water Samples

Most of the halogenated organic compounds found in nature are toxic, carcinogenic, and persistent. These compounds are harmful to the environment and need to be actively monitored to control environmental pollution. The sum parameter Adsorbable Organic Halogens (AOX) is the primary indicator for contamination of water, sediment, and soil by halogenated compounds. The AOX sum parameter combines organically bound compounds that contain chlorine, bromine, iodine, or fluorine atoms, which can be adsorbed onto activated carbon.

One of the most critical sources of AOX in the environment is the use of halogenated chemicals in industrial industries such as; pulp and paper and textile. Smaller quantities of AOX are also formed during the routine chlorination or disinfection of swimming pools and cooling water. Some of the used halogens react with organic matter to form organic halogen compounds, which may be discharged into the environment as effluent water or wastewater.

For many years AOX analysis by Microcoulometry was the accepted method for quantifying the halogen content in wastewater streams. The method consists of four main parts: collecting the organic halogens on activated carbon, washing with nitrate solution to remove interferences, combusting the carbon to form hydronated halogens, and quantifying the halogen content by microcoulometric titration. During the microcoulometric titration, the Cl^- , Br^- , and I^- ions react with the Ag^+ to precipitate, where F remains in the titration cell solution. This is why organic fluorides are not included as part of the AOX analysis.

By substituting the detection technique with Ion chromatography it makes it possible to include Fluorine as well as speciate between the different halogens. The Combustion IC enables the determination of individual halogenated compounds (fluoride, chloride, bromide, iodine) in aqueous matrices by a single analysis. Recently, several studies have focused on Perfluoroalkyl and polyfluoroalkyl substances (PFAS) found in aquatic systems and the environment. PFAS is a collective name for more than 6,000 potentially toxic substances that include a combination of fluorine compounds and alkyl groups. PFASs are water, grease, and dirt repellent. They are used in various products including lubricants, food packaging materials, extinguishing foam, and non-stick coatings on cookware, clothing, textiles, and cosmetics. PFAS are highly mobile once introduced into the aquatic environment and are not removed by conventional wastewater treatment. The presence of Adsorbable Organic Fluoride (AOF) in aqueous matrices is an important indicator of potential PFAS contamination. The analyzed amount of AOF in these samples provides insight into numerous PFAS precursors, which can transform into persistent PFAS that pollute the aquatic environment.

Sample Information	
Sample Type	Water
Component	Fluoride, Chloride, Bromide
Concentration	0 – 100 µg/L
Methods Applicable	-

Results – 10 µg/L Standard

Analyte	Spiked Concentration (µg/L)	Average (µg/L)	RSD (%) n=3	Recovery %
Fluoride in Demi water	10.0	9.9	4.6	99
Chloride in Demi water	10.0	10.1	4.3	101
Bromide in Demi water	10.0	9.2	1.1	92

Table 1 - Results for AOF, AOCl, and AOBr Analysis in DI water

Results – Spiked Samples

Analyte	Concentration (µg/L)	RSD (%) n=3	Spiked Concentration (µg/L)	Recovery %
Fluoride in Tap Water	2.8	14.7	10	106
Chloride in Tap Water	10.5	3.3	10	102
Bromide in Tap Water	9.5	1.1	10	105
Fluoride in Surface Water	6.9	9.6	25	100
Chloride in Surface Water	28.3	1.3	25	103
Bromide in Surface Water	30.0	6.2	25	103

Table 2 - Results for AOF, AOCl, and AOBr Analysis in Tap, and Surface Water

System Description

Sample Preparation – The organically bound halogenated compounds can be filtered and adsorbed onto activated carbon by the batch or column method. TE Instruments offers sample preparation systems for both adsorption methods. In this study, the column method was executed. The column method describes taking a 100 mL sample (water), and using 2 columns (in series) filled with activated carbon to adsorb organic halogens by filtration. After filtration, the inorganic content is rinsed off and the activated carbon is eventually combusted at a high temperature. The second column is to assure that the breakthrough of the sample does not exceed 10% of the total value. Results of the samples are obtained by summing the analyzed concentrations from the first and second column.

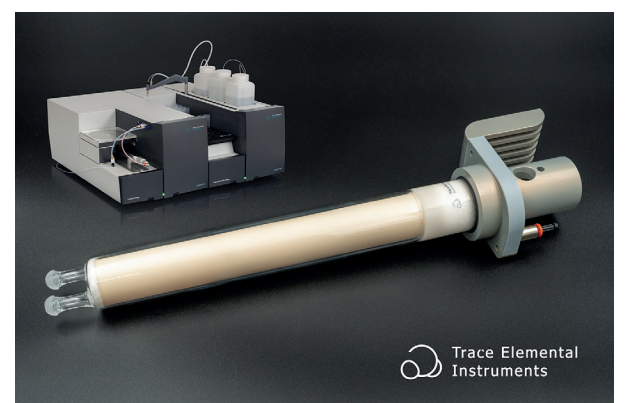
Introduction – The NEWTON solids autosampler automatically introduces the quartz cups carrying the activated carbon into the Boat introduction module. Once analyzed and cooled down, clean sample cups are retrievable from the clean cup container.

Combustion - The Combustion Unit is fitted with a dual-zone furnace. Every sample is completely oxidized by pyrohydrolytic combustion in an oxygen-rich environment at a high temperature. A unique feature of the Xprep C-IC setup is the option to use a furnace combustion tube including a ceramic insert. While standard AOX by MCD analysis focuses on Chlorine, Bromine, and Iodine, the analysis of AOX by C-IC has a wider focus including Fluorine. This is where the power of the ceramic insert is helpful. In a standard situation, Fluoride attacks quartz glass and may damage the combustion tube over time. The ceramic

insert protects the furnace tube quartz material, resulting in a far longer lifetime compared to a standard quartz glass set up.

Collection – After combustion, an absorber solution is added automatically to the output gas stream to guarantee complete absorption of analytes in the Fraction Collection Unit. In this process, the H-X and X_2 are converted to F-, Cl-, and Br-. These negatively charged ions will be separated in the IC column. To Up to 65 combusted samples can be absorbed and stored in the individual absorption vials. The combusted and collected samples can be transferred to the IC immediately or stored for later analysis. A re-run of combusted samples is possible at any time if desired.

IC-Injection – Once sample preparation has been finalized, the absorbent containing the analytes is automatically transferred from the Fraction Collection unit towards any renowned IC. A six-way-valve and 100 µL sample loop are by default integrated at the front of the Fraction Collection Unit. The internal syringe pump



loads and rinses the IC sample loop. The sample loop may be used to fill the pre-concentrator when present in the IC.

Calibration

Calibration standards are made from 4-Fluorobenzoic acid, 4-Chlorobenzoic acid, and 4- Bromobenzoic acid in DI water. All individual standards go through the complete process for each analysis: filtration (adsorption onto activated carbon), introduction, combustion, fraction collection, IC injection, and detection. Each calibration standard is analyzed three times.

Summary

The XPREP C-IC has been used to perform automated sample preparation of Combustion-IC analysis. The XPREP C-IC covers pyrohydrolytic sample combustion, fraction collection, and injection towards the IC. Water samples were pre-treated by the XPREP-3 filtration system to adsorb the organically bound halogens onto the activated carbon. Sample cups containing the activated carbon were introduced by the NEWTON solids autosampler into the boat-inlet system of the XPREP C-IC Combustion Unit. The activated carbon is combusted in an oxygen-rich environment at a high temperature. After combustion, the output gas stream containing the analytes is transferred to the Fraction Collection Unit and trapped in the absorber medium. Each individual analysis consists of sample filtration (adsorption onto activated carbon), combustion, fraction collection, IC injection, and detection. The IC provides accurate results with excellent repeatability (RSD) at trace level and good recoveries of targeted ions (F, Cl, Br) in spiked samples.

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The IC has been calibrated in the following ranges for the individual components:

Organic Component	Range	Regression - r ²
Fluoride	0 - 100 µg/L	0.9998
Chloride	0 - 100 µg/L	0.9998
Bromide	0 - 100 µg/L	0.9999

Table 3 - Calibration Range of Individual Halides

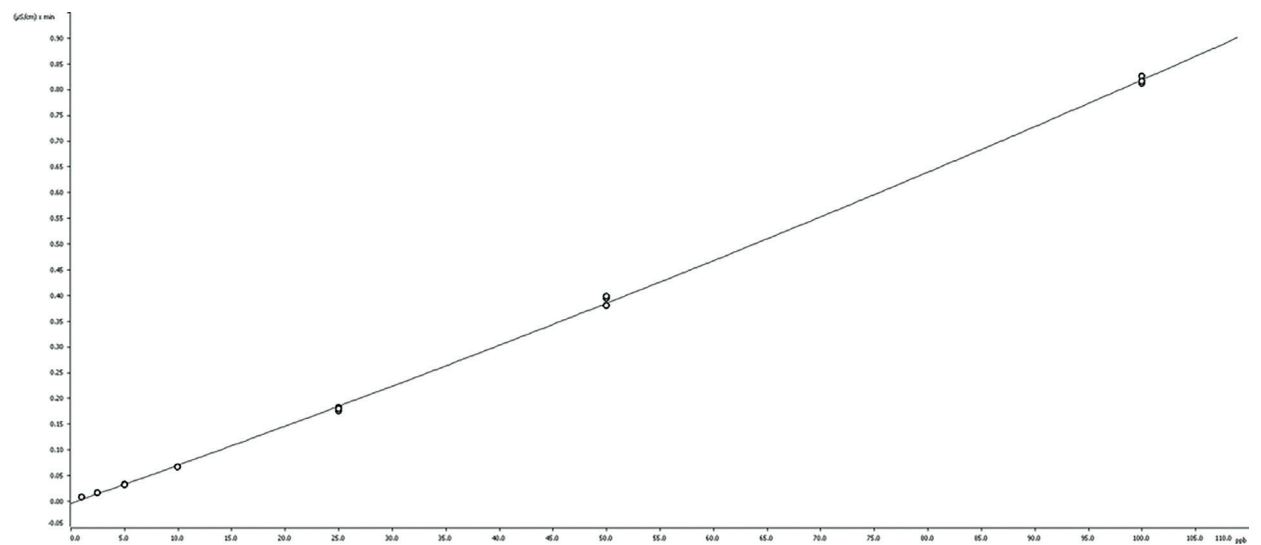


Figure 1 - Calibration line Bromide 0 - 100 µg/L - r² 0.9999

Example Chromatograms

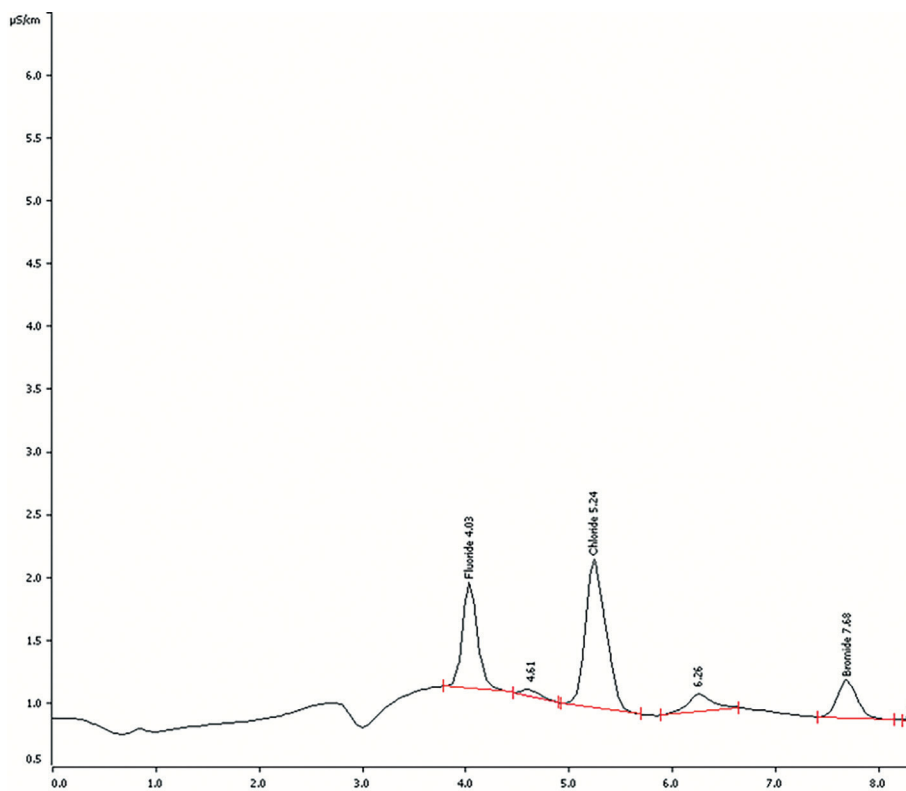


Figure 2 - Tab Water

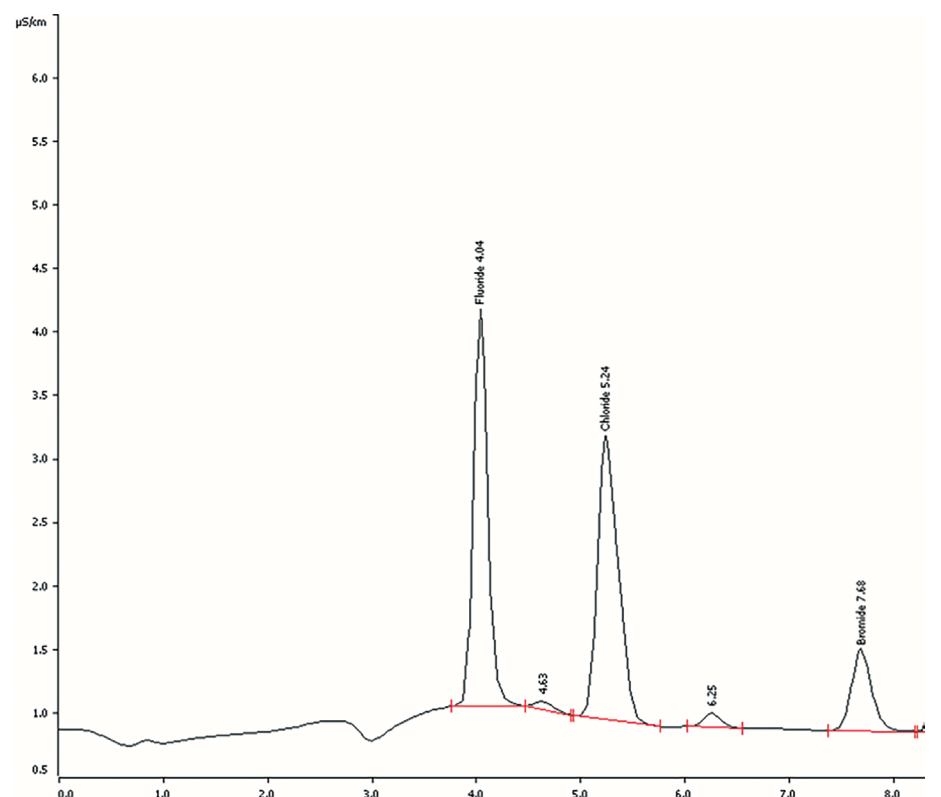


Figure 3 - Tab Water Spiked with 10 µg/L

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