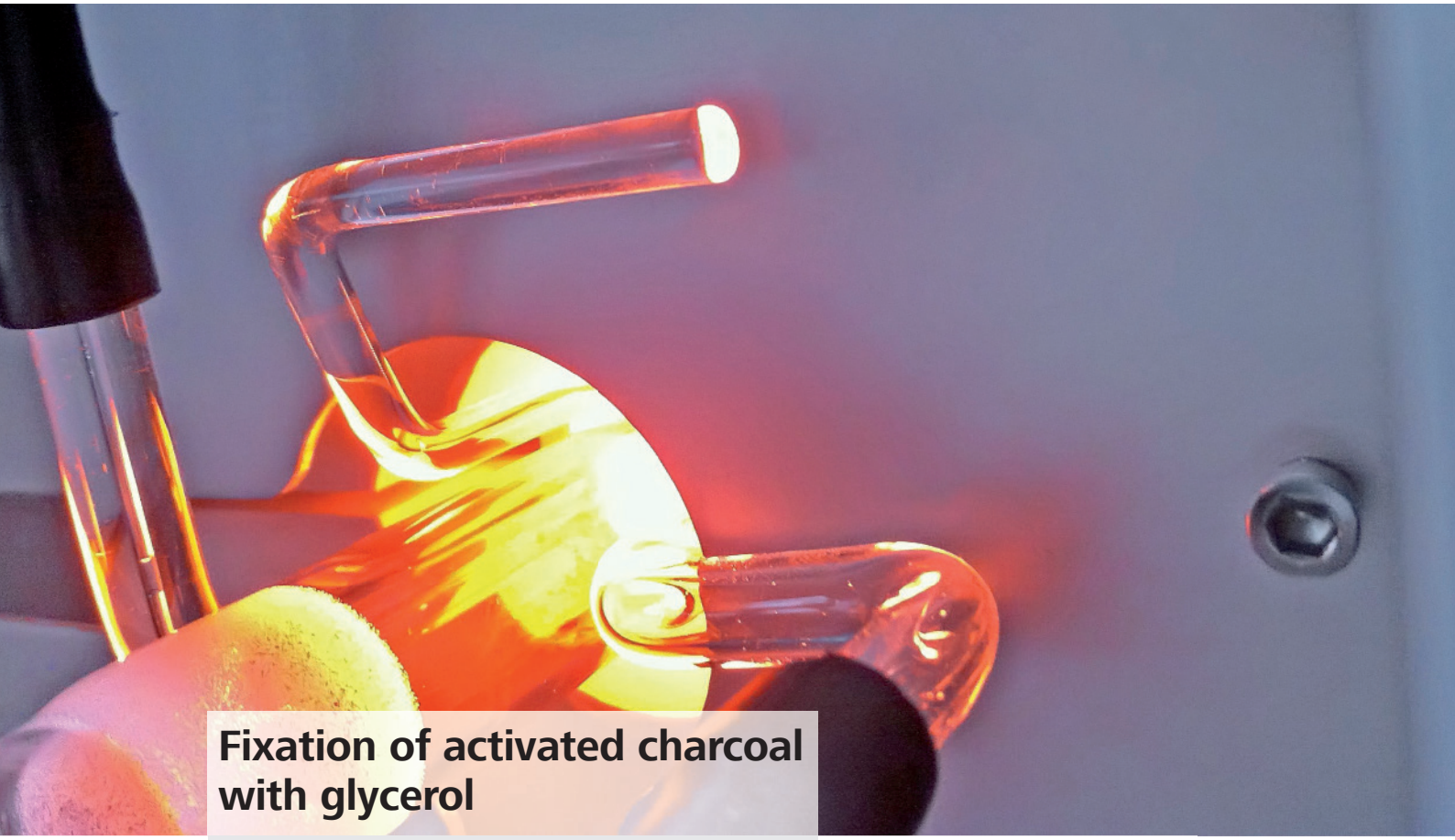
Measurement of AOX with combustion IC



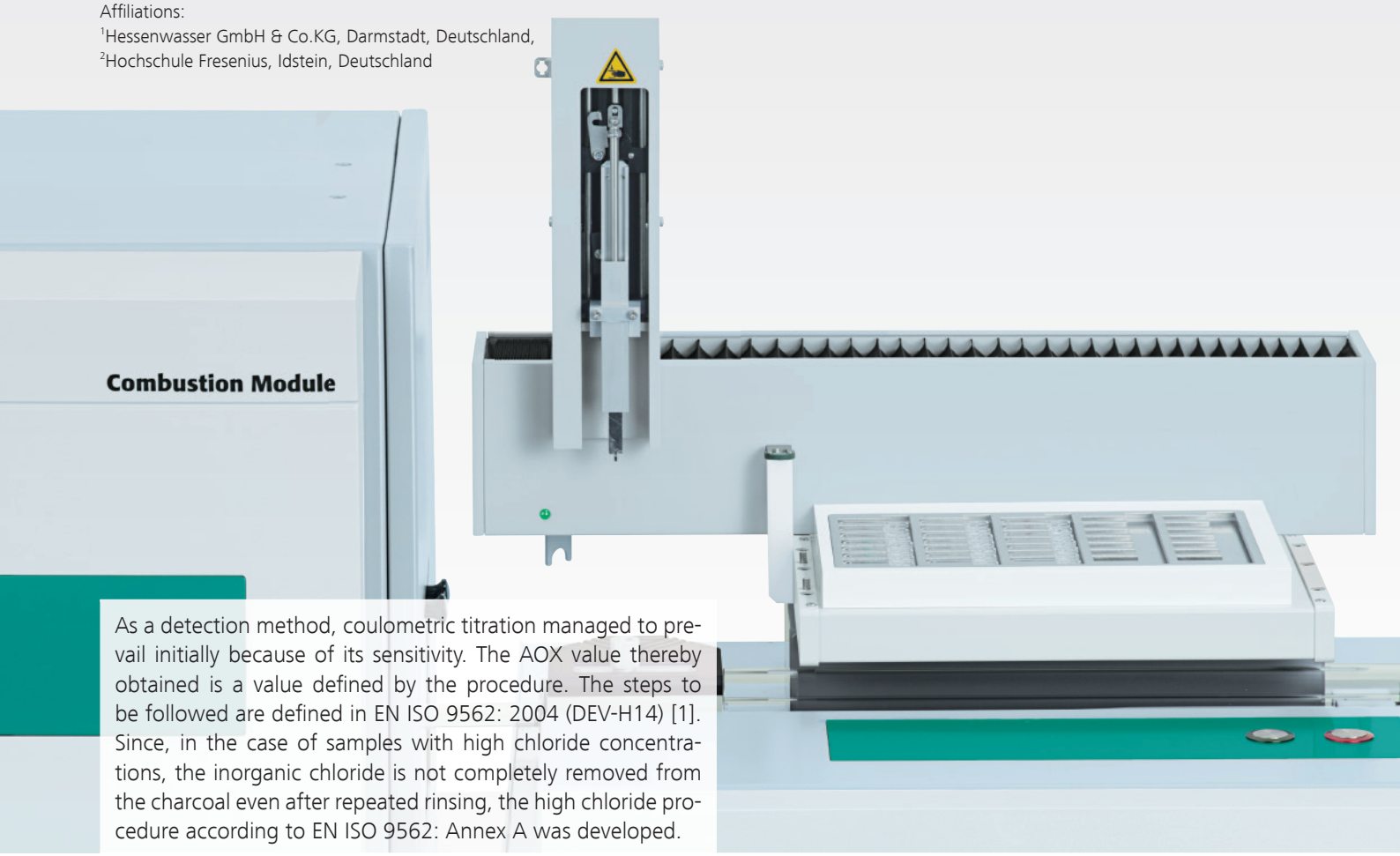
Fixation of activated charcoal with glycerol

Since the early 1990s, AOX has been an integral part of wastewater monitoring. It was developed as a sum parameter to describe the amount of (non-polar) chlorinated hydrocarbons. This type of substance can be easily enriched on activated charcoal. After combustion of this charcoal in an oxygen atmosphere, the resulting chloride is collected in an absorption solution. The content of chloride can then be determined by various techniques.

Metrohm International Headquarters; Herisau, Switzerland

Adrian Kaiser[2], Karl-Heinz Bauer[1], Karin Koch[1], and Konstantin Goettgens[1]

Affiliations:
[1]Hessenwasser GmbH & Co.KG, Darmstadt, Deutschland,
[2]Hochschule Fresenius, Idstein, Deutschland



As a detection method, coulometric titration managed to prevail initially because of its sensitivity. The AOX value thereby obtained is a value defined by the procedure. The steps to be followed are defined in EN ISO 9562: 2004 (DEV-H14) [1]. Since, in the case of samples with high chloride concentrations, the inorganic chloride is not completely removed from the charcoal even after repeated rinsing, the high chloride procedure according to EN ISO 9562: Annex A was developed.

Ion chromatography

As sum parameter for organically bound chlorine, organically bound bromine and iodine are also detected using coulometric AOX, without, however, any indication of their respective proportions. In the mid-1990s, the question of separating halogens and, in particular, measuring the content of organically bound iodine in various wastewaters emerged. As such, Oleksy-Frenzel et al. [2] combined preconcentration in activated charcoal followed by combustion and ion chromatography as a method for determining previously organically bound halogens (AOCl, AOBr, AOI).

With the evidence of perfluorinated compounds in the environment, the application field of the AOX method was finally extended for AOF determined by the highly sensitive ion chromatography [3]. In principle, it would also be possible to determine the proportion of organically bound sulfur. Unfortunately, this is not possible due to residual sulfur levels in commercially available activated charcoal.

In addition to the determination of organically bound halogens from aqueous matrices, this combustion method combined with ion chromatography as determination method has been increasingly used over recent years for the investigation of halogens and sulfur in various raw materials and industrial products.

Devices, chemicals, methods

To determine the levels of organically bound halogens in groundwater, surface water and wastewater samples are either pumped over activated charcoal columns (column method) or shaken with activated charcoal (shaking method).

For the enrichment using the column method, Hessenwasser uses a low-fluoride system (a1 Envirotech: Mitsubishi MCI TOX Sample Preparator and AOX Enrichment 30).

The combustion and determination is carried out with a device combination (Metrohm) [4], consisting of an autosampler, a combustion module, an absorber module and an ion chromatograph with chemical and CO_2 suppression as well as conductivity and UV detection.

The combustion in the oxygen stream is improved by the automatic addition of water (hydropyrolysis). In the case of AOF, AOCl, AOBr and AOI determination from aqueous matrices, ultrapure water is used as the absorption solution. For the analysis of most solids, 100 mg/L H_2O_2 is used as the absorption solution [5] and a pre-concentration column (Metrosep A PCC 2HC/4.0) is employed for the elimination of the matrix peak around fluoride.

The ion chromatographic separation is carried out on a high-capacity separation column (Metrohm A Supp 5 - 150/4.0, alternatively A Supp 5 - 250/4.0, guard column Metrosep A Supp 5 Guard/4.0). The eluent used is a solution consisting of 3.2 mmol/L Na_2CO_3 and 1.0 mmol/L $NaHCO_3$. The flow rate is set to 0.7 mL/min, while the injected volume of sample is 200 µL.

Table 1 provides the measured retention times for the halogen, nitrogen and sulfur species. The oxyhalide interferences mentioned in the table could not be observed in practice, presumably due to the sulfur content of the activated charcoal.

With the above-mentioned experimental conditions, detection limits of approximately 2 µg/L for AOF, approximately 5 µg/L for AOCl, and approximately 1 µg/L for AOBr and AOI could be reached in routine operation using commercial AOX activated coals with a sample volume of 100 mL and an IC injection volume of 200 µL. Through blank value optimizations (e.g., use of low-fluorine and low-chlorine charcoals) lower detection limits could be achieved.

Retention time in minute detector				Interference / Detector
Analyte	Conductance	UV 210	UV 226	
Fluoride	4.3			Iodate / Cond.
Iodate	4.4		4.5	Fluoride / Cond.
Chlorite	5.2			
Bromate	5.5	5.6		
Chloride	5.9			
Nitrite	6.7	6.8	6.8	
Bromide	8.2	8.2		Chlorate / Cond.
Chlorate	8.6			Br / Cond.
Nitrate	9.0	9.1	9.1	
o-Phosphate	14.2			
Sulfite	15.5	15.6	15.6	
Perchlorate	16.2			Sulfate / Cond.
Sulfate	16.3			Perchlorate / Cond.
Iodide	18.4		18.5	

Table 1. Retention times of the tested halogen, nitrogen and sulfur species on the Metrohm A Supp 5 - 150/4.0 column using an eluent consisting of a solution of 3.2 mmol/L Na_2CO_3 and 1.0 mmol/L $NaHCO_3$ at a flow rate of 0.7 mL/min.

Automated work

When using an autosampler, the activated charcoal in the sample boat will dry out upon prologed storage in the sample rack.

If the boat is then transported into the combustion module, care has to be taken to ensure that no charcoal from the sample boat is lost along the way. To avoid this inconvenience altogether, wetting of the charcoal extruded from the preconcentration columns with 2 drops of glycerol, applied with the aid of a pasteur pipette, has proven to be highly effective. The glycerol encapsulates the activated charcoal, so that it remains in the boat. **Figure 1** shows that the coal does not fall out even if the boat is turned upside down. As control measurements have shown, the p.a. glycerol used does not cause a blank value increase for the halogens. Repetitive measurements showed no change in the measured concentrations. Also, no drift was noticed as a factor of the time the samples were waiting on the autosampler prior to analysis.

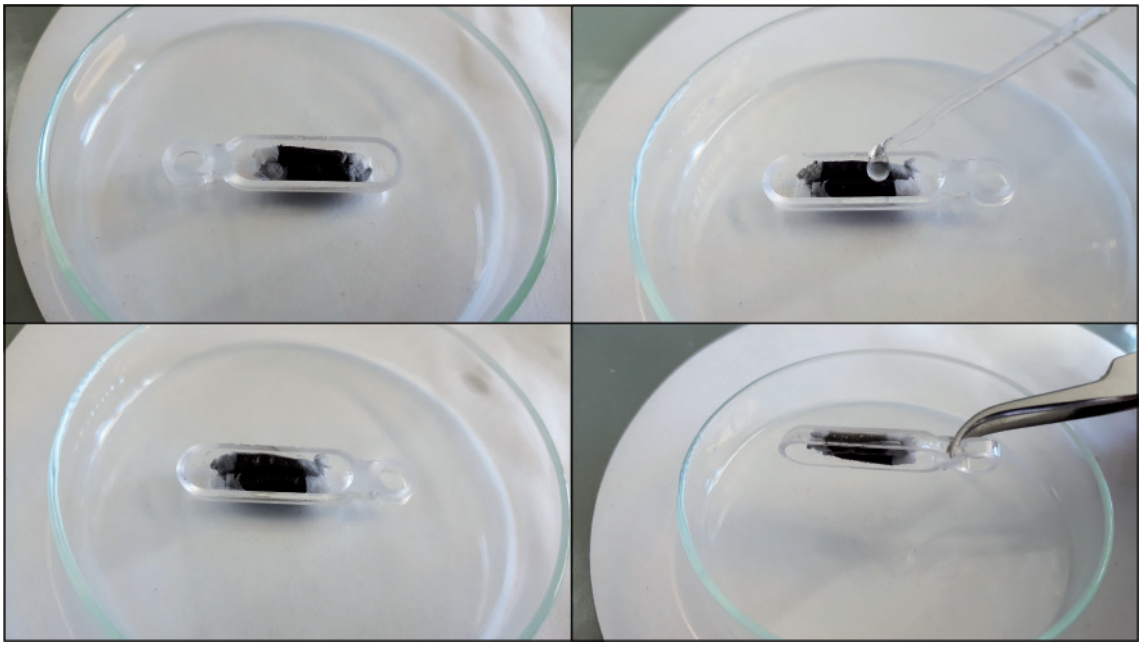


Figure 1. Top left: Extruded activated charcoal in the sample boats, Top right: Wetting with 2 drops of glycerol bottom left: wet activated charcoal. bottom right: after wetting the activated charcoal with glycerol, it does not fall out of the sample boat even when turned upside down. This effect persists for about 24 hours.

Overview

Fixing the charcoal with glycerol may help prevent potential interference from flying or dropping activated charcoal of automated Combustion IC (CIC) determinations. In general, Combustion IC is a well-suited method for notably increasing the information content from an AOX assay.

The shortcomings of the AOX may continue to pose a challenge (pretreatment of the sample, preconcentration behavior on charcoal due to varying polarity, presence of high contents of inorganic halogens). However, ion chromatography in contrast to coulometric titration provides much more information with regard to AOX analysis. Hence, determining a sum parameter for organically bound fluoride (AOF) besides the determination of AOCl, AOBr, and AOI is possible.

By conversion and addition, the AOX of the sample can also be calculated from the AOCl, the AOBr and the AOI (**Table 2**) content found. An extension of the measuring methods to the legally regulated range would be desirable, since with the determination of the newly standardized sum parameter AOF, a simultaneous determination of the AOX would also be possible.

	AOX measured	AOX calculated	AOF	AOCl	AOBr	AOI	
Plant discharge	21	20.8	1.4	16	4.2	10.4	µg/L
Sewage sludge	324	334	99.2	290	82.9	25.7	mg/kg

Table 2. Comparison of the measured AOX content in an sewage treatment plant discharge and a sewage sludge with the calculated content (addition of Cl equivalents) from the CIC determination.

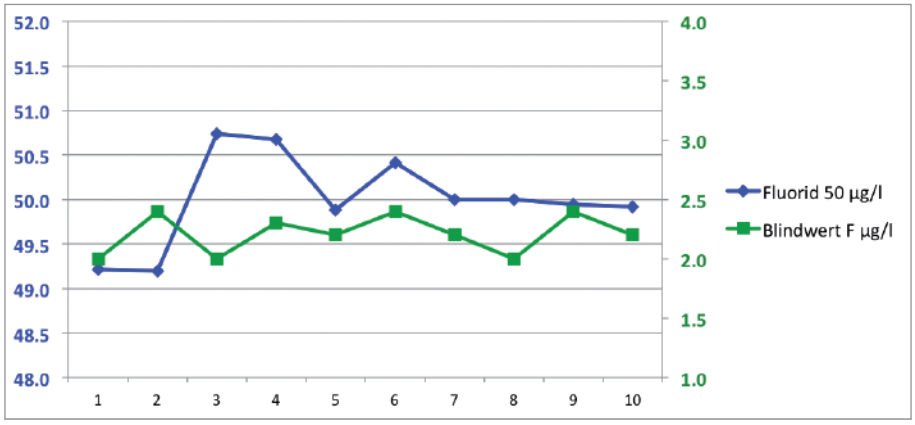


Figure 2. Concentration curve for 10 consecutive measurements of a fluoride blank (green) and a solution of 50 µg/L fluoride in the form of 4-fluoro-benzoic acid (blue).

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Contact: Dr. Karl-Heinz Bauer, Hessenwasser GmbH & Co.KG, Darmstadt, Deutschland