Challenge

The reliable determination of low AOX concentrations in groundwater and drinking water as well as in surface waters with suspended matter

Solution

An APU series sample preparation system with the AOX analyzer multi X 2500 for reliable routine analysis of AOX in groundwater, raw, drinking, and surface waters

Intended audience

Municipal waterworks, authorities for environmental protection and nature conservation, contract laboratories for environmental analysis

Determination of AOX in Raw, Drinking, and Groundwater, as well as in Surface Water in Accordance with ISO 9562

Introduction

Water that is open and unbound on the earth's surface is called surface water. This includes inland waters such as lakes, rivers, streams, springs, ponds, and reservoirs as well as coastal waters and seawater. These surface waters are used for various purposes: On the one hand as service waters in various industries (e.g., as cooling waters in industrial processes or as boiler feed waters in power plants) or as raw waters for the production of drinking water. Drinking water can also be obtained from groundwater, which is located below the earth's surface and is composed of percolated precipitation water and partially also of percolated surface water from rivers and lakes. The groundwater or surface water used to produce drinking water is referred to as raw water. After treatment by means of chemical (e.g., deferrization) and physical processes (e.g., filtration) in waterworks, it is fed into corresponding pipeline systems as ready-to-use drinking water and made available to consumers.

The use and monitoring of the quality of surface water, groundwater, and drinking water is regulated worldwide in numerous country-specific laws and regulations. For groundwater and surface water, fixed measuring points are usually installed for regular sampling, and close monitoring of biological, physical, and chemical parameters is established. Drinking water itself is one of the best-monitored foods in most industrialized nations. The list of chemical parameters to be monitored in the aforementioned waters is extensive and ranges from pH value to heavy metals and toxic organic substances, which are determined either as individual substances, group or sum parameters. This is also where the parameter adsorbable organically bound halogens (AOX) comes into play, which is often used as a screening parameter for estimating contamination with specific halogenated substances, such as pesticides.

The determination of AOX is an analytical convention that captures the sum of organically bound chlorine, bromine, and iodine (but not fluorine), which can be adsorbed on activated carbon under certain conditions. AOX components adsorbed on suspended solids are also included in the AOX result for unfiltered water samples. The parameter is determined in many countries, and the standardized method according to ISO 9562 is often used for this purpose. The application range of the method starts from 10 µg/L AOX. In very clean groundwater or drinking water, often lower concentrations of AOX are present. How these can be reliably determined is to be demonstrated on the basis of the analyses carried out. In addition, surface waters, which are sometimes heavily polluted with suspended matter, often pose a challenge for the AOX sample preparation used, since suspended solids can quickly clog the activated carbon used for adsorption. It is shown how, using the column method for enrichment, clogging problems and thus incorrect measurements can be reliably avoided.

Materials und Methods

Sample preparation was carried out according to the column method using the APU sim automatic preparation unit. The determination of the AOX was carried out with the multi X 2500. The analyzer was operated with a vertically arranged combustion tube made of quartz glass. Samples enriched on activated carbon columns were automatically fed to the combustion tube using the autoX 36 autosampler. Detection of the hydrogen halide compounds formed was performed microcoulometrically using the standard "sensitive" coulometer cell.

Samples and reagents

- Surface water, groundwater, and drinking water samples of different origin
- Control standard solutions of 4-chlorophenol in water with 10 µg/L and 20 µg/L AOX
- Pre-filled AOX columns (disposable tubes) with approx. 50 mg activated carbon each
- Concentrated HNO_3, 65%, for acidifying the samples
- Concentrated H_2SO_4, 96% for drying the gases at the AOX analyzer
- $NaNO_3$ stock and wash solution according to ISO 9562
- 0.01 mol/L HCl for functionality check of the AOX analyzer

Sample preparation

All water samples were acidified to a pH ≤ 2 with concentrated HNO_3 immediately after sampling and stored in the refrigerator at approx. 4 °C until their measurement. Just before the AOX determination, the samples were mixed with nitrate stock solution according to ISO 9562 (5 mL stock solution per 100 mL sample) and filled into the syringes of the APU sim. At a rate of 3 mL/min, 100 mL of this solution was pumped through two activated charcoal columns arranged in series. This enrichment process was followed by an automatic rinsing process of the columns to remove inorganic chloride from the activated carbon. For this purpose, the columns were rinsed with 25 mL of the nitrate washing solution according to ISO 9562. Due to the expected low concentrations of AOX, no prior dilution of the samples was carried out.

Table 1: Settings for column method

Parameter	APU sim settings
Adsorbed sample volume	100 mL
Volume of nitrate washing solution	25 mL
Adsorption and rinsing rate	3 mL/min

Calibration

Since the microcoulometry used to detect the AOX is an absolute detection method, calibration of the AOX analyzer is not necessary. To check its functionality, the coulometric measuring cell is tested with 0.01 mol/L HCl. For this purpose, 50 µL of this hydrochloric acid is injected directly into the coulometer cell using a microliter syringe. In doing so, 17.73 µg ± 0.53 µg chloride should be detected by the system. Another way to check the AOX analyzer is to combust the 0.01 mol/L HCl. For this purpose, 50 µL of the hydrochloric acid are injected onto a quartz tube filled with ceramic wool and introduced into the analyzer's furnace. The recovery for chloride should be within the same limits as for direct injection of the HCl into the measuring cell. Furthermore, AOX analysis involves a daily check (every working day) of the overall procedure. For this purpose, AOX control standards are first adsorbed on activated carbon and then combusted and detected in the analyzer. According to ISO 9562, the measured value of the control standard should not deviate by more than 10% from the theoretical value, which means a recovery rate of between 90% and 110%.

Instrument settings and method parameters

Prior to the determination of the AOX in the water samples, blank value determinations as well as measurements with control standards were carried out. The sample preparation for the total of 18 samples and 3 blank values was completed within approx. 3.5 hours. This is possible because the APU sim used for this purpose can adsorb and rinse six samples with a volume of 100 mL simultaneously within approximately 45 minutes. Parallel to the sample enrichment, the analyzer was put into operation and measurement was started for the first completely prepared samples.
During the combustion of the loaded activated carbon columns, the organic halogen compounds were converted to gaseous hydrogen halides (HX). After drying the combustion gases using concentrated sulfuric acid, the HX gases were transferred to the microcoulometric measuring cell. The standard coulometric cell used has a wide working range from 1 µg to 100 µg chloride, which can be extended if necessary. The sensitivity of the standard measuring cell was sufficient for the water samples examined.

Table 2: AOX analyzer settings

Parameter	multi X 2500 settings
Furnace temperature	950 °C
Titration delay	360 s
Maximum titration time	600 s
Coulometer cell temperature	21 °C
Carrier gas	Oxygen 99.995%
Working range of coulometer cell "sensitive"	1 µg to 100 µg Cl^-
Extended working range	10 ng to 1000 µg Cl^-
Automation	autoX 36

Results and Discussion

The analytical results of all tested waters and the control standards are summarized in Table 3. The measurements were carried out as duplicate determinations for each sample.

Table 3: Results of the AOX determination

Sample description	Blank value AOX [µg Cl^-]	Determination 1 AOX [µg/L]	Determination 2 AOX [µg/L]	Average value AOX ± SD [µg/L]	Relative Standard Deviation RSD [%]
Groundwater 1	0.35	7.5	8.1	7.8 ± 0.42	5.4
Groundwater 2	0.35	9.3	9.9	9.6 ± 0.42	4.4
Drinking water 1*	0.35	5.4	4.8	5.1 ± 0.42	8.3
Drinking water 2*	0.35	2.8	3.2	3.0 ± 0.28	9.4
Surface water 1 (lake)	0.35	20.4	19.5	20.0 ± 0.64	3.2
Surface water 2 (river)	0.35	19.1	19.2	19.2 ± 0.07	0.4
Surface water 3 (creek)	0.35	12.9	14.0	13.4 ± 0.78	5.8
Control standard 10 µg/L AOX	0.35	10.2	9.6	9.9 ± 0.42	4.3
Control standard 20 µg/L AOX	0.35	19.5	19.9	19.7 ± 0.28	1.4

* Sample was adsorbed with 200 mL on the activated carbon.

The results prove that the AOX can be determined with very good reproducibility in waters with low concentrations of organo-halogen compounds. The variation of the measured values in the double determinations was less than 10% relative standard deviation in all samples. This is an excellent value for the low contents of ≤ 20 µg/L AOX, which on the one hand underlines the detection strength of the analyzer used and on the other hand demonstrates the suitability of the column method carried out with the aid of the APU sim. The surface waters contaminated with suspended matter also showed no abnormalities during the adsorption and rinsing step. The suspended particles were collected on the fixing material for the activated carbon, and thus did not pose any risk for the fine-grained carbon becoming clogged. Due to the low AOX load, the drinking water samples were enriched with 200 mL sample volume, which could easily be applied with the help of the APU sim by simply filling the syringes manually twice in succession. The subsequent rinsing step was again performed automatically.

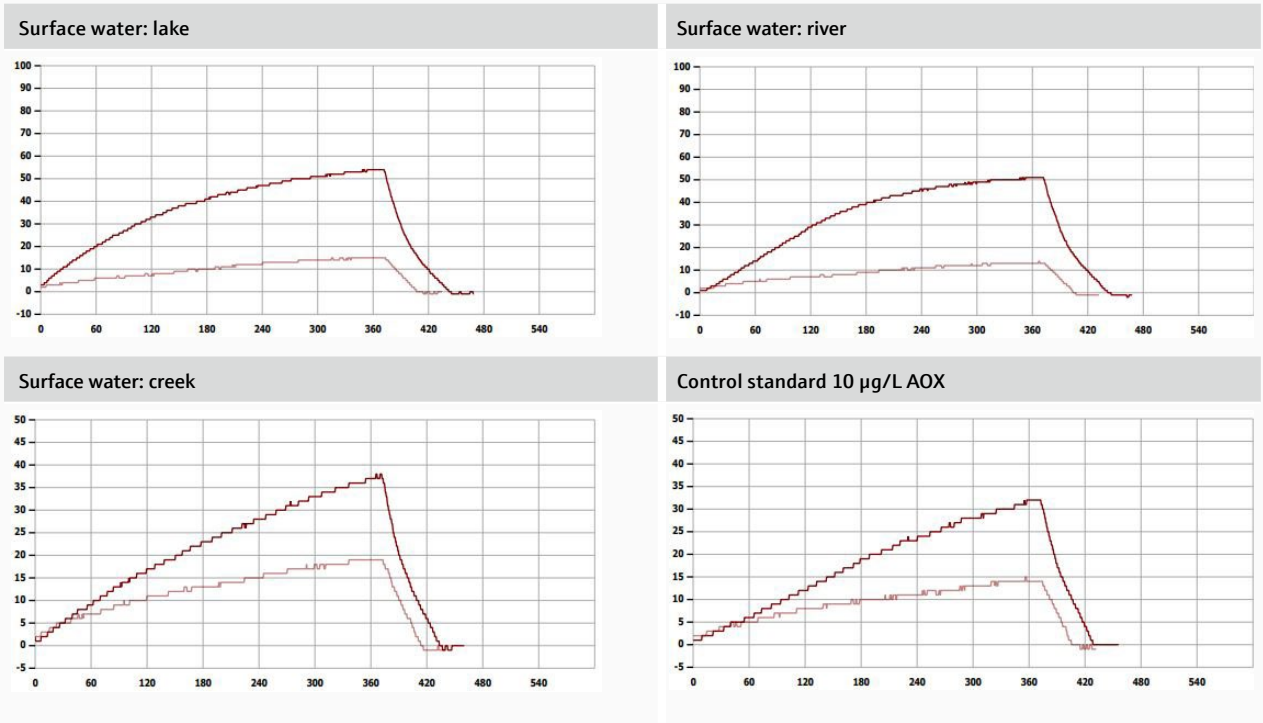

Figure 1: Typical AOX measurement curves of selected samples

Figure 2: multi X 2500 with autoX autosampler

Figure 3: APU sim

Summary

The measurement results obtained show that sample preparation using the column method with subsequent measurement on the multi X 2500 provides reproducible AOX results for various types of low-polluted water. Even samples with AOX contents of < 10 µg/L can be prepared and measured effortlessly using an increased sample volume (200 mL). The APU sim sample preparation unit is characterized by easy handling and fast processing of up to six samples simultaneously. In combination with the AOX analyzer multi X 2500, measurement results are thus quickly available, which is particularly advantageous for small sample series. Laboratories with a high number of AOX samples can also use sequential sample preparation units, such as the APU 28 connect, which can process up to 28 samples (also for the determination of SPE-AOX) fully automatically (e.g., overnight).
Compared to the time-consuming and labor-intensive batch method, AOX analysis by the column method is not only cost-effective, but also robust, reliable, and very well suited for water samples of all kinds.

Recommended device configuration

Table 3: Overview of devices, accessories, and consumables

Article	Article number	Description
multi X 2500	450-126.430	AOX/TOX, EOX, POX analyzer
multiWin software	450-011.803	Control and evaluation software
autoX 36	450-126.412	Autosampler for multi X 2500
APU sim	450-900.300	Automatic sample preparation unit
Set 100 disposable tubes filled, 18 x 6 mm	402-880.610	Activated carbon tubes for AOX determination by column method

References

ISO 9562:2004 Water quality - Determination of adsorbable organically bound halogens (AOX)

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Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

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