

Publication

Sum Parameters

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- Pharmacy
- Cosmetics
- Material Analysis
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Determination of Organically Bound Halogens

Meet increasing demands with the new multi X[®] 2500

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Introduction

Over 20 years ago, the determination of the parameter AOX (adsorbable, organically bound halogens) found its way into the Deutschen Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (German Unified Procedure for Water, Waste Water and Mud Analysis), and has since gained considerable importance. The procedure is now defined by the international norm ISO 9562. Outside Europe, primarily in North America, additional procedures have been established for the determination of organically bound halogens - e.g. ASTM methods and EPA guidelines. Nevertheless, corresponding administrative regulations or guidelines do not exist in many European countries, including within the EU. At the same time, the interest in the determination of summary material parameters is increasing in regions outside Europe, particularly in Asia.

The original application area of AOX analysis is the analysis of surface water, groundwater and drinking water. The contribution of these methods to the monitoring and, therefore, improvement of the surface water quality is undisputed and generally recognized.

The following strong orientation towards waste water analysis has consistently stimulated the criticism of this "sum parameter" and prompted very controversial discussions, and also raised the question of the practicality of the unlimited application of this analysis method.

The ecotoxicological meaning of this parameter cannot always be clearly assessed because, in addition to the detected AOX-relevant substances in water, other substances can also be found that are not of anthropogenic origin, but of biogenic origin, of low solubility or inert, e.g., PVC. Therefore, not all relevant substances are detected because of the various adsorption behavior of the halogen compounds. Furthermore, pure fluorine compounds cannot be detected because of the argentometric procedure. Also, not all AOX-relevant compounds can be classified as ecologically critical. With industrial and commercial waste water, users have observed a partial failure of the AOX method, although the procedure is judged viable for the majority of samples.

Overall, the AOX determination is a method defined by convention that is subject to very complex influencing factors and has been supplemented by additional procedures for the detection of organically bound halogens, such as SPE-AOX (AOX after solid phase extraction), EOX, (extractable organic halogen compounds), POX (organic halogen compounds that can be blown out), among others. Up to now, all of these procedures have made an essential contribution to reducing the environmental impact with organic halogen compounds, and will continue to do so in the future.

Fundamentals and demands of measurement technology and instrumental information

The following items form the fundamentals of all procedures for the determination of organically bound halogens:

1. A corresponding enrichment of the organic substances (adsorption, extraction, expulsion).
2. The mineralization of organic compounds in a combustion system at temperatures near 950°C in an oxygen stream.
3. The subsequent microcoulometric detection of the halogenated hydrocarbons formed during combustion, with specification of the result in relation to chloride.

Although the fundamental for determination of relevant parameters (AOX, SPE-AOX, EOX, POX) has not experienced a change over the last several years, the device technology has adapted to the modified and very different requirements of the routine laboratory. In smaller laboratories, the primary focus has been on flexibility in order to prove the laboratory's value with a wide range of products in the analysis field. Preference is placed on systems that can quickly and cost-effectively determine various parameters. As a part of an integration of small laboratories into a laboratory network, specific analysis methods are frequently centralized at one location. Measurement technology specialized in a specific parameter is typically used in these laboratories and the quick throughput of large sample series is in the spotlight. Some instrument manufacturers have taken on these demands and can offer analyzers that can be used for the determination of organically bound halogens, both flexibly and oriented towards high throughput.

Sample preparation

AOX determination frequently begins with a sample preparation that is unfortunately time-consuming. In accordance with DIN EN ISO 9562, three methods are fundamentally available for the enrichment of organic substances with activated carbon: the stirring method, batch method and column method. Use of the respective method should be carried out based on the sample. In reality, laboratories are frequently heavily focused on the use of only one procedure largely due to specific administrative regulations.

The batch method can be used for all samples types (water with and without particle loading, solids) and is preferably implemented with sludge and water samples with a large number of particles. In routine operation, the low degree of automation of the filtration process following agitation of samples, and the resulting high manual effort for the AOX sample preparation, have a negative effect on the sample throughput and the costs of the analysis. Improvements can be made with semi-automatic filtration equipment, which can be used to simultaneously prepare several samples for the analysis. When compared to the typically used polycarbonate membrane filters, the use of alternative filter materials offers additional advantages with regard to a shortened filtration period with difficult matrices.

The automatic filtration equipment AFU 3 can be used with the advantages described for fast sample preparation using the batch method.



AFU3 – fast AOX sample preparation using the batch method

The sensitivity of the batch method compared to higher concentrations of inorganic chloride, which cannot be completely removed from active carbon during the washing process with nitrate rinsing solution following adsorption, is also common knowledge. Higher results of AOX are the analytical aftereffect. The column method offers several advantages compared to the batch method: higher chloride concentrations up to 1 mg/l have a less negative effect on the subsequent analysis, the risk of contamination is overall lower because the carbon is, for the most part, prevented from coming into contact with the environment. Furthermore, the completeness of the adsorption can be checked at any time with a simple comparison of the charging of the active carbon columns that are placed next to each other. Last but not least, the column method is characterized by a high degree of automation. The column method can be used for the sample preparation of all aqueous samples, even with the presence of particles. These samples are typically collected on a filter tube connected in series to the active carbon columns and can thus be loaded into the combustion without negatively affecting the adsorption step with a potential obstruction of the carbon tube. Many users have recognized the advantages of the column method and successfully established this method in their routine. In larger AOX laboratories, above all, there is an increasing demand for sample preparation systems that can simultaneously guarantee high sample throughput and very low maintenance requirements. The device series APU 28, for example, meets this demand. Up to 28 samples can be automatically prepared in succession according to the column method. A two-canal version (APU 28S) equips the device for two samples simultaneously, thereby doubling the speed of sample preparation. The omission of complicated valve technology makes this device concept easy to maintain. Automatic systems are now also available for the SPE-AOX procedure

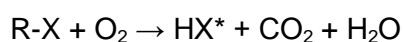
(DIN 38409 - 22, DIN EN 9562, Appendix A), which was previously seldom used due to the high manual effort required in practice. The so-called SPE-AOX is used with difficult matrices - e.g. with samples with very high chloride contents and low AOX concentrations. With the APU 28 SPE, a fully automated sample preparation can be completed, which allows enrichment on SPE columns, elution with methanol and subsequent adsorption on active carbon with no manual intervention. Soxhlet extraction with solid samples (DIN 38414 – 17, Draft 03-2004) has become established for sample preparation for EOX determination. Alternatively, extraction by ultrasound, or by stirring a sample in suitable solvents, is used to some extent.



APU 28S: high sample throughput with the column method

Sample feeding and combustion

After successful preparation, the samples are loaded into the actual OX analyzer. It is assumed that the organic halogen compounds are fully converted to halogenated hydrocarbon, carbon dioxide and water in an oxygen stream at temperatures of at least 950°C.



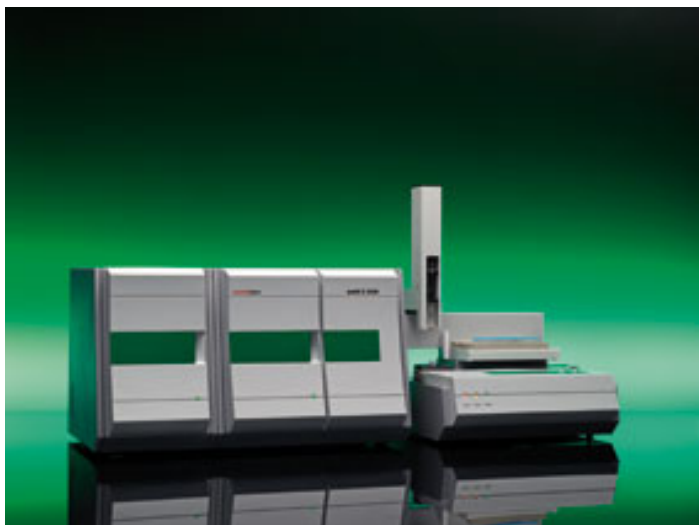
*(HCl, HBr, HJ)

The pyrolysis gas is dried with concentrated sulfuric acid.

Combustion can occur either in a vertical oven system or a horizontal oven system. Both techniques have different advantages. Vertical systems are characterized by a space-saving design and, typically, simple automation, above all for the AOX column method. Horizontal systems have the advantages of a controllable and, ideally, controlled, combustion that benefits the analysis of EOX extract, in particular, via a slow sample supply.

The multi X[®] 2500 is a system that combines both techniques and, thereby, all advantages. Equipped with the Double Furnace Technology, an integrated tilting furnace ensures a simple changeover between the oven fitting positions. Therefore, a very flexible system is available for smaller laboratories for a wide variety of applications and fast parameter changes. At the same

time, the analyzer can be specially operated and optimized for high sample throughput for the determination of only one parameter.



multi X® 2500 AOX analyzer in horizontal operation mode

In rare cases, users report on incomplete combustion - particularly with EOX determination, and, to some extent, with AOX determination in sludge. Removing the aftereffects (formation of soot) interrupts the work process and entails additional costs. Techniques that exclude the formation of soot are desirable in everyday laboratory practice. Flame sensor technology makes a valuable contribution in this regard.

The monitoring of the flames formed during combustion of organic extracts or solid samples, and the feedback on the speed of the sample introduction into the hot zone of the oven, enables a controlled and quantitative combustion. The multi X® 2500 can be equipped with this technology. Users whose routine tasks include, in addition to AOX, SPE-AOX, EOX, the determination of POX, total halogen/total chlorine in solids (e.g. in primary or derived fuels) and TOC in aqueous samples can use the multi X® 2500 for these tasks. For an automatic sample feed, a single autosampler can take on all these tasks (POX determination is an exception). The variable design of the sample rack and "feeding tools" (syringes, gripper, ejection tool) enables a quick adjustment to the corresponding measurement task.



Transporting the charged active carbon to the oven using the autoX 112

Detection

The halogenated hydrocarbons formed during the combustion process are absorbed in an electrolyte and argentometrically determined as halide ions. Microcoulometry is the most common procedure.

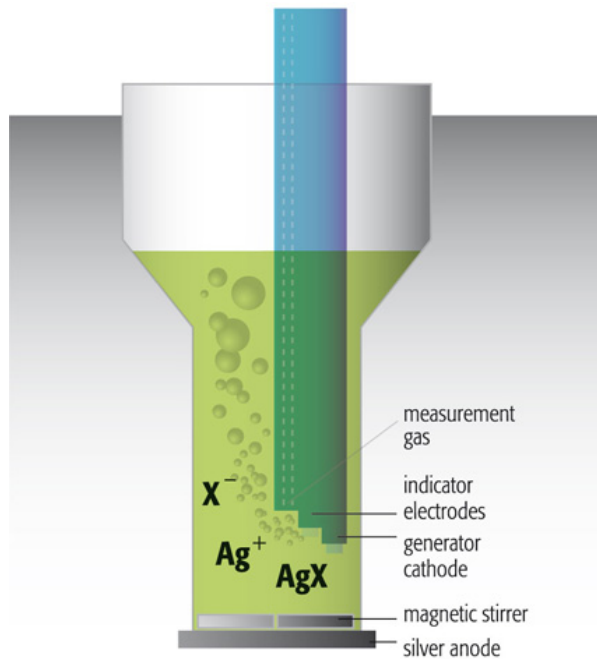


The silver ions required for the halide precipitation are electrolytically generated on a silver anode. The silver ion concentration in the electrolyte increases after the quantitative conversion of the halide generated during the combustion. This moment is the titration end point, which can be detected using a polarized indicator electrode pair (biamperometric) or a potentiometric indicator electrode. Using Faraday's laws, the halide quantity is calculated from the charge amount up to the complete conversion of the analyte. The result is specified in relation to chloride.

The detection typically displays the most sensitive part of the OX analysis system that regularly requires maintenance and care. Electrolyte changes and cleaning one or more electrodes are a part of everyday laboratory practice. Solutions that reduce maintenance requirements to a minimum have proven themselves in practice for many years. This includes, for example, the so-called combination electrode, which combines a generator cathode and indicator electrode pair in a single electrode body. Many users appreciate fast operational readiness with minimum care. The combination electrode can be used for a wide range of applications and is predestined for routine AOX determination in the concentration range between 10 µg/l and 1 mg/l (without sample dilution). For particularly high concentrations of halogens, this electrode can be optionally

expanded tenfold, in combination with a large electrolyte volume, in a special measuring cell ("high-concentration" cell) within your range of application. This is particularly advantageous for the direct determination of halide in solid matrices.

The potentiometric indication is preferred for particularly small halide concentrations, as is the case with the majority of EOX samples in routine analysis. The multi X[®] 2500 offers the possibility of using both the combination electrode (indication using the amperometric procedure) and potentiometry.

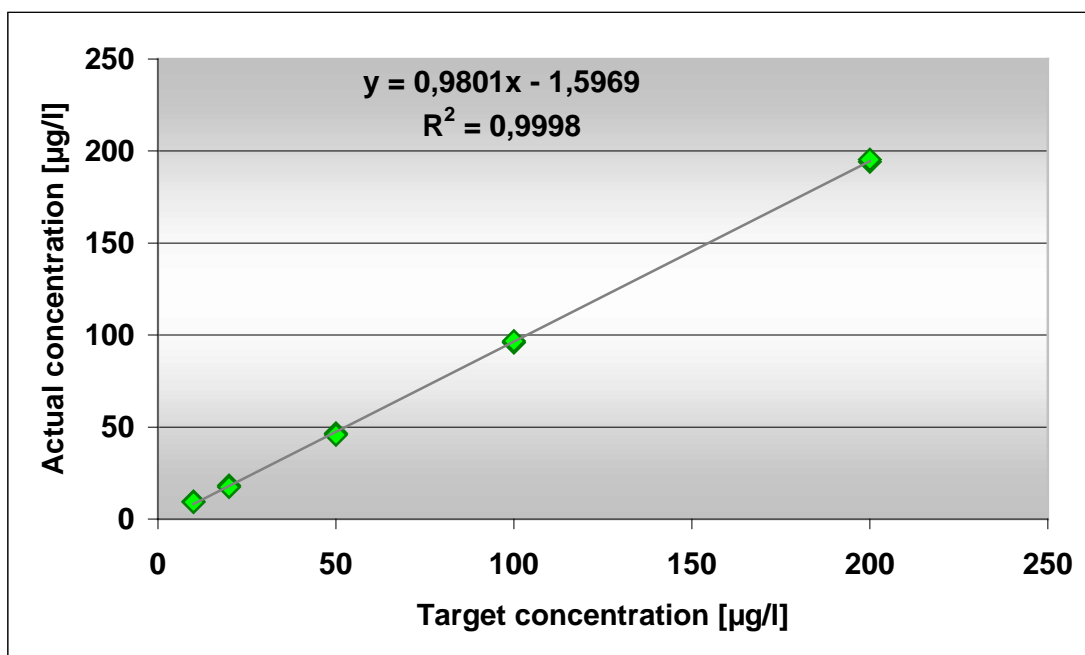


Low-maintenance detection using the combination electrode

Measurement examples

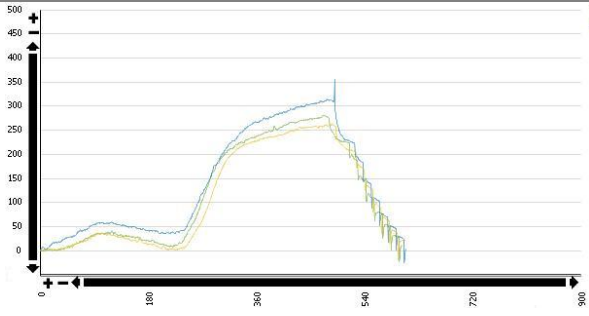
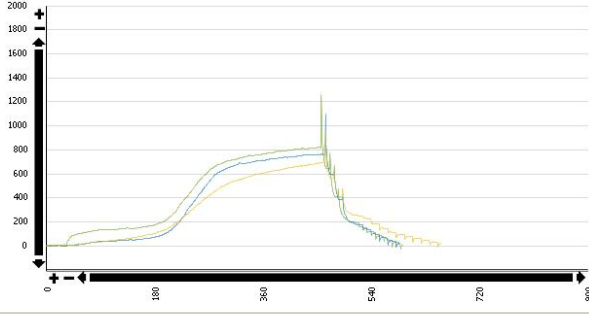
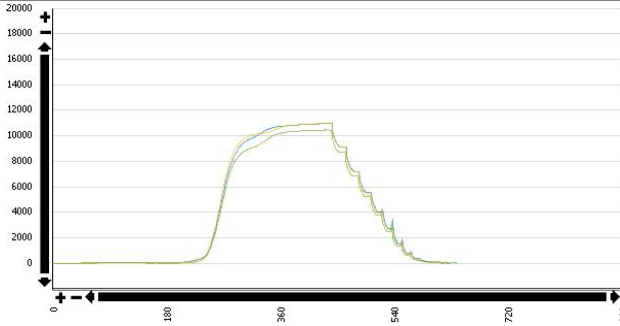
Despite modern measurement technology, reproducible measurement results are not always a matter of course. A variety of quality control measures are available to support the user in his search for possible causes. The majority of users are fully aware that the AOX procedure should not be used with certain sample types. Nevertheless, modern analysis systems with integrated monitoring functions give the user the security for routine analysis with reliable results.

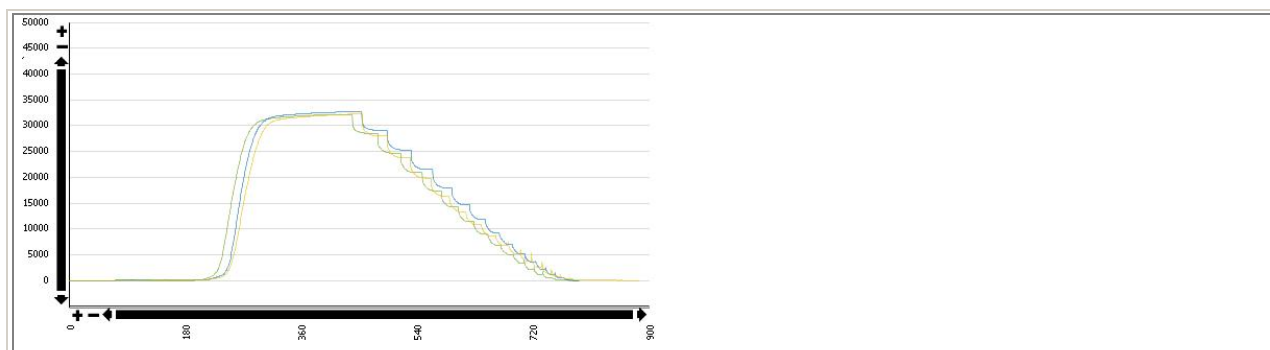
Thus, for example, a basic test is routinely conducted for the AOX determination, whereby five defined AOX standards are typically measured and correlated with their nominal values. For this, specific requirements for the slope of the correlation straight line (between 0.95 and 1.05) and the correlation coefficient (> 0.999) must be fulfilled.



AOX recovery function generated with the multi X[®] 2500

In routine analysis, the detection of very small OX contents (typically with EOX measurements of low loaded samples) frequently poses many more problems than the detection of halide contents above 1 µg absolute. A controlled combustion, paired with a very sensitive detection, can significantly increase the reproducibility of the results, even in lower concentration ranges.

Sample description	Absolute mass Cl	EOX concentration
Water sample 1	0.046 µg	0.46 mg/l ± 0.04 mg/l
		
Water sample 2	0.131 µg	1.31 mg/l ± 0.13 mg/l
		
Contaminated sludge	1.518 µg	463 mg/kg ± 8.0 mg/kg
		
Sample from abandoned polluted areas	4.300 µg	1059 mg/kg ± 9.9 mg/kg



Measurement examples of different EOX samples with multi X[®] 2500 (duplicate measurement)

Summary

Taking into consideration the limits of the procedure, analysis methods are available along with the AOX determination and derived versions. With a justifiable expenditure, these analysis methods can relatively quickly provide statements on the loading of aqueous and solid samples with a variety of organic halogen compounds of various origin, which frequently have unknown identities and effects.

In a world that is becoming increasingly aware of major environmental problems and, in particular, the monitoring of water quality, one can assume that the thoroughly unpopular and not undisputed parameter AOX, including its derived methods, will also find its place in the future.

Last but not least, it is comparatively fast, simple and inexpensive to determine. Selecting the optimal analysis technology can support the user in cost-efficient completion of routine analysis of organically bound halogens.

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