Application Note · multi X 2500

Challenge

Typically, the parameter POX is determined using an AOX analyzer, which must be adapted for this purpose. A quick change between AOX and POX analysis is required.

Solution

The versatile multi X 2500 AOX analyzer can be quickly converted for the determination of POX, making it ideally suited for the analysis of organically bound halogens of all kinds.

Intended audience

Industrial water and wastewater laboratories, wastewater treatment plants, environmental protection authorities, contract labs

POX Determination in Water Samples

Introduction

The parameter POX is used for the determination of purgeable organically bound halogens. The substance group of purgeable organically bound halogens primarily comprises volatile halogenated hydrocarbons. These are defined as halogenated C1 and C2 hydrocarbons, such as dichloromethane or vinyl chloride. Freons (i.e. chlorofluorocarbons, also known as CFCs) also belong to the class of volatile halogenated hydrocarbons. However, the use of CFCs is prohibited in many applications, as the use of volatile halogenated compounds is strictly regulated in general. For example, many volatile halogenated compounds are used in cleaning and extraction plants, in the textile industry, or in the surface treatment of a wide variety of materials. This happens under special conditions to limit emissions. Other volatile halogenated compounds are used as precursors for the synthesis of other products, such as vinyl chloride in PVC production. Despite numerous laws, bans and regulations, volatile halogen compounds continue to enter our environment in various ways (e.g., through improper recycling of old refrigerators), resulting in contamination of soil and water.

In addition to the determination of individual volatile halogenated hydrocarbons, so called sum parameter analysis is also used in practice. POX is one such sum parameter and is used to quickly estimate a hazard potential as a starting point for further compound-specific investigations or as a screening parameter. POX can usually be determined using an AOX analyzer, which is available in many water laboratories, used to determine adsorbable organically bound halogens. While the procedure for AOX determination is described in various international standards (e.g., DIN EN ISO 9562), the determination of POX is often only established as an internal laboratory procedure (SOP). All determination methods are based on purging/stripping the water sample with an inert gas, usually argon. For this purpose, the water sample is heated to a specific temperature in a suitable gas wash bottle. The expelled halogenated hydrocarbons are transferred in a gaseous state to a furnace, where they are digested at temperatures

≥ 900 °C in an oxygen stream and converted to hydrogen halides. These are then detected in a microcoulometer cell. A POX analysis is always useful if many volatile halogenated substances are suspected in the water sample, which may not be detected in AOX determination. The results of both parameters together (POX and AOX) then allow a better assessment of the hazard potential of the analyzed sample. If both parameters can be determined using just one and the same analyzer without major modifications or adjustments, this is a great advantage for routine analysis.

Materials and Methods

POX was determined using the multi X 2500 AOX analyzer. The analyzer was operated with a vertically arranged combustion tube made of quartz glass. The formed hydrogen halide compounds were determined coulometrically using the sensitive cell. The samples were heated to 60 °C in a commercially available water bath.

Samples and reagents

- Stock solution (dichloromethane in ultrapure water) with 22.2 mg/L POX content
- 3 water samples: two different process waters, one treated wastewater

Sample preparation

Sampling should be carried out by filling cleaned glass bottles (500 mL nominal volume) to the brim and sealing them tightly. The POX content should be analyzed immediately after sampling. Further sample preparation is generally not necessary. If there are high concentrations of volatile halogenated hydrocarbons in the sample and/or substances that form explosive mixtures are suspected, it is advisable to dilute the sample before determination.
The POX stock solution should also be prepared on the day of measurement. Proceed as follows: approximately 30 mL methanol is placed in a 50 mL volumetric flask. Using a microliter syringe, 0.5 mL of dichloromethane is added and the volumetric flask is then filled up to the mark with methanol. Then, about 490 mL of ultrapure water is placed in a graduated flask with a nominal volume of 500 mL and 1 mL of the prepared methanolic dichloromethane solution is dosed directly under the water surface. The flask is then filled up to the mark with ultrapure water.

Calibration

As the microcoulometry used to detect POX is an absolute detection principle, the analyzer does not need to be calibrated. To check its functionality, the coulometric measuring cell is tested with 0.01 mol/L HCl solution. For this purpose, 50 µL of this hydrochloric acid is injected directly into the coulometer cell using a microliter syringe. The system should detect 17.73 µg ± 0.53 µg chloride.
The POX stock solution is now used to check the functionality of the POX analyzer as a complete system. For this purpose, a POX bottle is almost completely filled with ultrapure water and placed in the water bath. Directly before starting the measurement, 1 mL of the POX stock solution is injected under the water surface and the POX attachment is immediately placed on the bottle. The recovery should be 22.2 ± 2.22 µg chloride.
The water bath was set to 60 °C to heat the samples at a constant temperature in the water bath. The water bath was placed at the right side of the analyzer. The sample volume was 150 mL in each case, for which a special, volume-calibrated POX glass bottle was filled with sample to the brim.

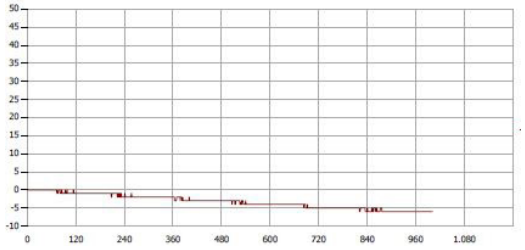
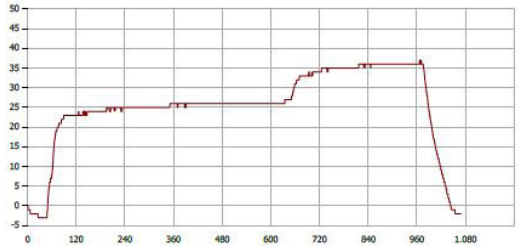
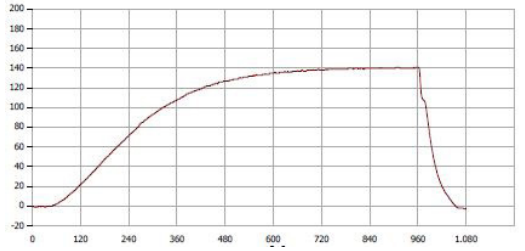
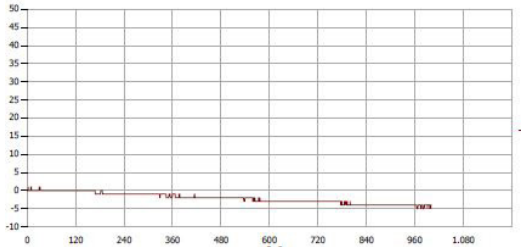
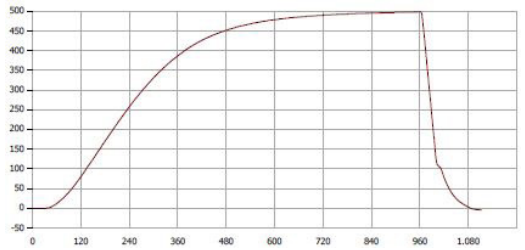
Table 1: Settings on the multi X 2500 for POX determination

Parameter	Specification
Furnace temperature	950 °C
Titration delay	60 s
Purge time	900 s
Purge flow (Ar)	250 mL/min
Required gases	Oxygen 99.995%, argon 99.996%
Temperature coulometric cell	21 °C
Working range of sensitive cell	1–100 µg Cl

Results and Discussion

Before determining the POX in the water samples, blank value determinations and measurements with the POX stock solution were carried out. The analytical results and measuring curves of all samples tested are summarized in table 2.

Table 2: Results of the POX determination with multi X 2500

Sample ID	Result POX	Measuring Curve
Blank POX	0.00 µg Cl	
Process water 1	9.5 µg/L	
Process water 2	29.3 µg/L	
Wastewater, treated	0.00 µg/L	
Stock solution POX 1 mL contains 22.2 µg Cl^-	20.7 µg Cl (recovery rate = 93%)	

The measurement curves are typical for POX samples without abnormalities and prove that the purging time of 900 s was set sufficiently high. This can be recognized by reaching a signal plateau, which occurs after about 12 to 13 min in all samples and did not change significantly until the end of purging after 15 min. The titration of the halide ions accumulated in the coulometric measuring cell progresses rapidly (rapid signal drop at the end of the measurement curve) and is completed within one to two minutes, depending on the POX content.

Summary

The POX measurement is quick and easy to perform. It should be noted that both, the temperature of the sample during purging and the purge flow (argon flow rate), as well as the selected time have an influence on the POX result. On the vertically configured mutli X 2500, the change from AOX to POX mode can be carried out within a few minutes. To do this, only the gas lock (a glass component) must be replaced at the inlet of the combustion tube, which can be done without tools even when the furnace is hot. The combustion tube itself stays inside the furnace. Practical plug-in connections (so-called FAST connectors) enable the POX bottle, including the attachment containing the sample to be analyzed, to be connected to the gas circle quickly and safely. A POX method can be selected via multiWin software, which allows guided measurement of the samples in a user-friendly manner.
The multi X 2500 analyzer is characterized by a high degree of flexibility in terms of application options (AOX, TOX, EOX, POX) and the high flexibility regarding the degree of automation.

Figure 1: multi X 2500 in vertical configuration with autoX 36 AOX autosampler

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 data evaluation software
POX kit	450-889.620	Accessory module for POX determination
Water bath	Lab supplies	For tempering POX samples

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