Challenge
Can an AOX analyzer, which is predestined for the determination of AOX in water samples, also determine total chlorine and organically bound chlorine in pulp and paper?

Solution
With the flexible AOX analyzer multi X 2500, pulp, paper, recycled paper, as well as wastewater from the paper industry can be analyzed quickly and precisely.

Intended audience
Recyclers of waste paper, producers of pulp, paper, and cardboard

Determination of Total Chlorine and Organically Bound Chlorine in Pulp, Paper, and Secondary Pulp According to ISO 11480 with an AOX Analyzer

Introduction

Worldwide, the demand for paper is increasing every year, and the proportion of waste paper used for paper production is rising steadily. The main component of all paper and cardboard grades is the so-called pulp. This can be obtained from wood or plants (e.g., straw, hemp) or is produced by processing waste paper (pulping and washing or de-inking). It is referred to as recovered or secondary pulp, secondary or recycled fiber, which is mainly used for production of recycled papers. If the pulp for paper production is rich in cellulose and contains only small amounts of lignin, it is referred to as chemical pulp, which is the product of a chemical pulping process. Higher proportions of lignin in the pulp make the paper brittle with aging and cause yellowing, so these are removed by a bleaching process. Bleaching was traditionally carried out with chlorine gas, but this has now been replaced by other bleaching processes in many places due to its high environmental impact. Today, for example, bleaching with chlorine dioxide and hypochlorite or with oxygen-rich compounds, such as hydrogen peroxide or ozone, are the main methods used. The use of chlorine-containing bleaching agents produces a not inconsiderable quantity of organic chlorine compounds, the majority of which are found in the process wastewater. However, some of the chlorine compounds also end up in the final product, the paper. The contents of total chlorine and organically bound chlorine thus represent an important quality characteristic for the paper and provide information about the manufacturing and bleaching process. If a paper is labeled „ECF" (= elemental chlorine-free), this means that the bleaching process was carried out without chlorine gas, but with the help of other chlorine compounds. The label „TCF" (= total chlorine-free) indicates that the paper was bleached with the help of oxygen-rich compounds and completely without the use of chlorine compounds.
Papers can also have a wide variety of quality seals, which provide information on either the raw materials used and/or

the manufacturing or bleaching process. For example, papers that bear the German „Blue Angel" quality seal are made from 100% waste paper and with a chlorine-free bleaching process.
Monitoring the content of total chlorine and organically bound chlorine in the intermediate pulp/secondary pulp and the final product paper/recycled paper is thus of great importance for both, manufacturers and consumers. An international standard procedure, ISO 11480, describes how to carry out the analysis, for which two techniques are basically available. First, combustion of the samples in a quartz tube at high temperature followed by microcoulometric determination of the hydrogen chloride formed, and second, sample digestion according to Schöniger with subsequent detection of the chloride formed by means of ion chromatography. The microcoulometric method has many advantages for the user, such as a high degree of automation and a high degree of safety in the combustion of the samples. This will be described in more detail below, using the example of the analysis of different paper grades.

Materials and Methods

The AOX analyzer multi X 2500 was used in its horizontal configuration to determine the levels of total chlorine and organically bound chlorine.

Samples and reagents

- Hydrochloric acid, 0.01 mol/L, for checking the performance of the coulometer cell
- Sulfuric acid, 98%, for drying the combustion gases
- Acidic nitrate solution, working solution, prepared from acidic nitrate stock solution (17 g $NaNO_3$ +1.4 mL 65% HNO_3 + dist. water, 1 L) by dilution 1:20 with dist. water, to wash the samples for the determination of organically bound chloride.
- 2-chlorobenzoic acid, 250 mg/L Cl, as aqueous reference solution (diluted) and for spiking of paper samples
- Activated carbon for the determination of the organically bound chloride
- Polycarbonate filter, pore size 0.45 µm, diameter 25 mm
- Dried paper and recycling paper samples

Sample preparation

For the determination of the total chlorine content, the paper samples were first coarsely crushed with the aid of tweezers and scissors and then ground in a ball mill. Approximately 10 to 30 mg of the samples prepared in this way were weighed directly into a quartz boat for analysis with the multi X 2500.
The determination of the organic chlorine content requires the removal of the inorganically bound chlorine (chlorides) by an extraction/washing step prior to combustion. For this purpose, the crushed samples were weighed into Erlenmeyer flasks (250 mL capacity) and 100 mL of the acidic nitrate working solution and 15 mg of activated carbon were added. The sample weights were again in the range 10 to 30 mg. After sealing the Erlenmeyer flasks, they were shaken vigorously on a laboratory shaker for one hour. The samples were then filtered through polycarbonate filters, which were washed with approx. 25 mL of the nitrate working solution and sucked almost dry. The filters were now placed on sample boats made of quartz glass and fed to the furnace of the analyzer.

Calibration

Calibration of the analysis system is not necessary, since coulometric detection is an absolute detection method.
A 0.01 mol/L HCl was used to check the functionality of the coulometer measuring cell. Of this, 50 µL was dosed directly into the cell using a microliter syringe, and the mean ± SD obtained was 17.5 ± 0.3 µg chloride for a double determination. This meets the requirements for recovery in the range ± 5% of the nominal value according to ISO 11480.
The overall procedure (enrichment on activated carbon + combustion + detection) was checked using aqueous control standards of 2-chlorobenzoic acid previously enriched on activated carbon. Again, the recovery averaged 96%; a range of 91% to 110% is required according to ISO 11480.

Instrument settings

All samples were placed in quartz boats after appropriate sample preparation. These boats were automatically fed to the furnace by means of an automatic boat drive (ABD). This process was controlled by a flame sensor, which automatically regulates the feed rate based on the intensity of the combustion. This ensures safe, controlled sample evaporation and combustion and prevents the formation of soot and other incomplete combustion products.
The combustion of the samples took place in two phases. In the first phase, the sample was heated to 1,050 °C in an argon atmosphere, resulting in vaporization of the volatile and pyrolysis of the low-volatile organic compounds. The gaseous products were completely converted to hydrogen chloride (HCl) and other reaction products (CO_2, H_2O, ...) in an oxygen-rich atmosphere. In the second stage of the process, the combustion tube was completely flushed with oxygen to ensure that all non-volatile pyrolysis products were converted into the analyte of interest. The combustion gases were dried with concentrated sulfuric acid and finally transferred into a microcoulometric titration cell for chlorine determination.

Method Parameters

All samples were analyzed using a so-called TX method for solids. The process parameters are summarized in Table 1.

Table 1: Process parameters

Parameter	Setting
Furnace temperature	1,050 °C
2nd combustion time	60 s
Ar (1st phase)	100 mL/min
O_2 (main flow)	300 mL/min
O_2 (2nd phase)	100 mL/min
Feed rate of the sample	Automatically controlled by flame sensor

Evaluation parameters

The evaluation of the measurement signals and calculation of the results was carried out fully automatically by the analyzer's user-friendly multiWin control and evaluation software.
The measuring range of the microcoulometric measuring cell "sensitive" used extends from 1 µg to 100 µg chloride. The use of an even more powerful coulometer cell ("high sensitive") or a cell for extremely high chloride concentrations ("high concentration") is possible at any time with the multi X 2500, but not necessary for the application described here. The settings documented in Table 2 were made for the coulometer cell "sensitive".

Table 2: Detection parameter

Parameter	Setting
Max. integration time	1,200 s
Cell temperature	23 °C
Titration delay	240 s

Results and Discussion

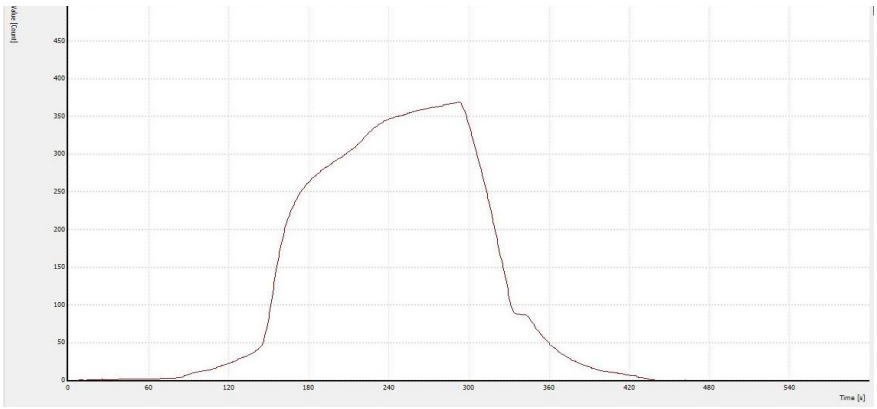
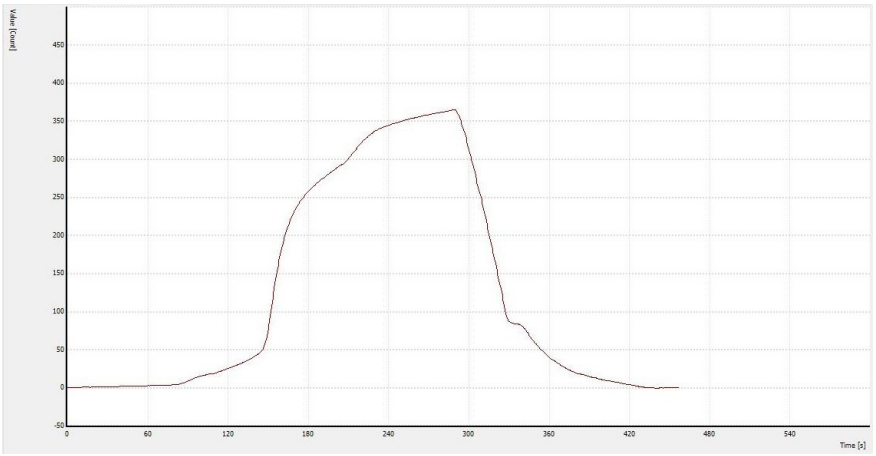
The measurements for the total chlorine determination and for the determination of the organically bound chlorine were each carried out as a duplicate determination in accordance with ISO 11480. The measurement of the samples was preceded by a blank determination. The blank values for the organically bound chlorine content were subjected to the same pretreatment procedure as the samples themselves. Blank values and measurement results as well as the standard deviations obtained for the samples and the control standards are listed in Table 3. The blank values are already put into account when stating the measurement results.

Table 3: Measurement results - Determination of total chlorine and organically bound chlorine contents

Sample ID	Concentration total chlorine ± SD	Concentration organically bound chlorine ± SD
Blank	< 1 µg	1.1 ± 0.1 µg
Paper (ECF)	865 ± 25 mg/kg	693 ± 19 mg/kg
Paper (TCF)	412 ± 10 mg/kg	73 ± 3 mg/kg
Recycling paper	623 ± 17 mg/kg	332 ± 15 mg/kg
Control standard, 100 µg/L Cl	-	96 ± 2 µg/L

The results obtained illustrate that both the total chlorine content and the content of organically bound chlorine in different paper grades can be determined reliably and reproducibly using the combustion method and subsequent coulometric detection with the multi X 2500 AOX analyzer. According to the requirements of ISO 11480, the individual values of a double determination must not deviate by more than 10% from the mean value. This criterion is fulfilled for all samples/ determinations. The average measurement time is approx. 8 min.

Table 4: Example measuring curves total chlorine and organically bound chlorine

Sample	Measuring curve Cl
Paper TCF – Total chlorine	
Recycling paper – Organically bound chlorine	

Conclusion

While two analytical steps are necessary for digestion according to Schöniger and subsequent detection of the halogens by means of ion chromatography, the method presented here has the advantage of combining digestion and detection in only one analytical step in a single system. The combustion controlled by the flame sensor is always complete, incomplete digestion and thus sooting is reliably prevented. Combustion followed by coulometric detection also offers the advantage of a high degree of automation, which can significantly increase sample throughput for routine laboratories. The large dynamic measuring range of the coulometer allows the determination of both, low and high concentrations of total chlorine and organically bound chlorine. Since the contents of bromine and iodine in pulp and paper are often negligible, the effects on the determination of chlorine content by coulometry can usually be ignored. Other system components such as the auto protection system and a heated transfer line ensure a high level of work safety and reliable results.
Furthermore, in addition to chlorine determination in solid samples such as pulp, paper and cardboard, the AOX analyzer multi X 2500 can also be used to determine the AOX content in wastewater from the paper industry in accordance with ISO 9562.

Figure 1: multi X 2500 with autoX autosampler

Recommended device configuration

Table 5: Overview of devices and consumables

Article	Article number	Description
multi X 2500	450-126.430	AOX analyzer for determination of AOX, EOX, POX, TX, and other parameters
Extension kit for multi X 2500	450-889.610	Necessary for horizontal operation
Automatic boat drive (ABD)	450-126.416	Necessary for horizontal operation
autosampler autoX 112	450-126.690	Necessary for automated operation for solid samples
Sample rack 35 positions	450-889.523	Sampler tray for quartz boats
Quartz boats with downholder	402-889.673	Advantageous for handling polycarbonate filters

References

ISO 11480: 2017-05, Pulp, paper and board – Determination of total chlorine and organically bound chlorine

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