Challenge
Separate determination of inorganically and organically bound chlorine species using a single analyzer, without time-consuming sample preparation

Solution
The multi EA 5100 enables the direct, simple, and rapid determination of various chlorine species without further sample preparation

Intended audience
Refineries, ethanol/bio-ethanol producers, fuel testing laboratories

Determination of organically and inorganically bound chlorine in ethanol according to ASTM D4929 method B

Introduction

Fuels are subject to strict controls regarding their chemical composition and physical properties. The chemical composition has a direct impact on the performance and longevity of engines and, consequently, on exhaust emissions into the environment. Modern, more environmentally friendly fuels are characterized by a high ratio of ethanol, which is derived from renewable raw materials. For many years, typical fuel blends with corresponding volume percentages of ethanol have been in use: E5, E10, E15, and, increasingly in some regions and countries, E20. Just like the fossil fuel component of the blend, the ethanol component is tested for a wide variety of impurities. In this context, the element chlorine also plays an important role, as its corrosive properties can damage production facilities, storage tanks, and, not least, combustion engines. Both inorganic and organic chlorine compounds should be present only in trace amounts in ethanol and the final fuel blend.

The ASTM D4929 standard describes three possible methods for determining the content of organically bound chlorine in the naphtha fraction of crude oil, which is the fossil component used in the production of a high-quality gasoline blend. In all three methods described, the naphtha is first washed several times with water to remove inorganically bound chlorine; after which the remaining content of organically bound chlorine (OCl) in the naphtha is determined. If one wishes to directly determine the content of organically bound chlorine in the pure fuel additive ethanol, the washing procedure described above cannot be used, since ethanol and water are highly miscible. However, an indirect method allows for a very simple and rapid determination of OCl even in this case. By measuring the total chlorine content (TCl) and the proportion of inorganically bound chlorine (ICl) the OCl can be calculated. The proportion of organically bound chlorine is the difference: OCl = TCl – ICl. In practice, the expected

concentrations of OCl are often very low, and the primary focus is on the proportion of inorganically bound chlorine (ICl). The multi EA 5100 offers a solution for the direct measurement of inorganic chloride. The results obtained are comparable to those of an ion chromatography system.

The following section demonstrates how to determine the total chlorine content (TCl) in ethanol according to method B of ASTM D4929, using oxidative combustion followed by the detection of the chloride ions formed during this process via micro-coulometry. The multi EA 5100 combustion elemental analyzer is used for this purpose, it also allows for a very fast and simple determination of inorganically bound chlorine (ICl) in ethanol.

Materials and methods

All tests were conducted using a multi EA 5100 Cl. The device was equipped with a chlorine module and the high sensitive cell.

Samples and reagents

- Ethanol sample
- Calibration standard solutions A for TCl (50% OCl + 50% ICl), c = 1 mg/L, 2 mg/L, 5 mg/L, and 10 mg/L Cl from 2,4,6-trichlorophenol and HCl in ethanol
- Calibration standard solution B for ICl, c = 10 mg/L Cl from HCl in ethanol
- Control standard solution A, c = 12.6 mg/L Cl (5.7 mg/L ICl + 6.9 mg/L OCl), prepared from 2,4,6-trichlorophenol and HCl in ethanol
- Control standard solution B, c = 10 mg/L Cl from HCl in ethanol

Sample preparation

The ethanol sample was analyzed directly without any further sample preparation.

Calibration

The calibration to determine the total chlorine content (TCl) was performed using four different concentrations of calibration standard solution A. For this purpose, 100 µL of each concentration was injected into the furnace of the multi EA 5100 analyzer. Each concentration was analyzed at least twice. The resulting calibration curve (Fig. 1) was evaluated using linear regression, taking into account the blank value of the solvent (ethanol) when calculating the slope and the y-intercept. The achieved limit of quantification was 0.1 mg/L, and the correlation coefficient was 1.

An additional calibration for the direct determination of the concentration of inorganically bound chlorine (ICl) was performed as follows: Calibration standard solution B was dispensed directly into the coulometric measuring cell of the multi EA 5100 analyzer using a microliter syringe. Five different volumes were injected: 20 µL, 40 µL, 60 µL, 80 µL, and 100 µL; at least one duplicate determination was performed for each aliquot. The limit of quantification was 0.2 mg/L, and the correlation coefficient was 1. The calibration curve is shown in Figure 2.

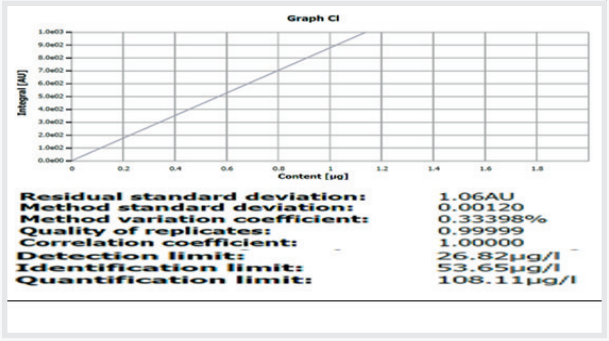


Figure 1: Calibration curve TCl (furnace measurement)

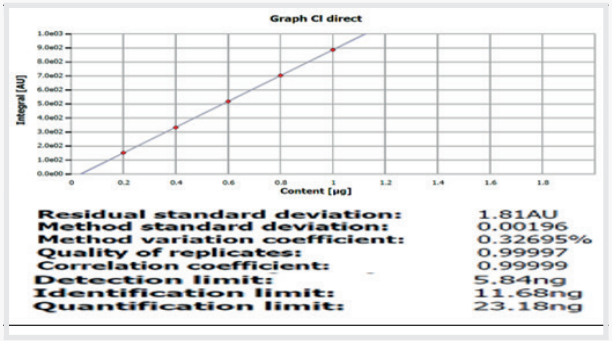


Figure 2: Calibration curve ICl (cell direct measurement)

Instrument settings

For all measurements, a multi EA 5100 equipped with a chlorine detector with high sensitive cell was used.
To determine the TCl content via combustion, an injection volume of 100 µL was used for both samples and standards. Sample digestion was performed using an efficient, catalyst-free high-temperature combustion process in a quartz tube. The combustion process takes place in two phases. In the first phase, the volatile sample components are vaporized in a stream of inert gas (argon), followed by the combustion of the resulting gaseous products in an oxygen-rich atmosphere. In the second phase, the heavier, non-volatile sample components and the resulting pyrolysis products are quantitatively oxidized in pure oxygen. The resulting reaction gases are then dried and transferred to the measuring cell, where the hydrogen chloride formed is absorbed in the cell electrolyte. Chlorine is quantified by micro-coulometric titration. A built-in auto-protection system and heated transfer lines ensure maximum operational reliability (particle and aerosol trap) and complete transfer (no condensation loss) of the generated HCl gas.
To determine the concentration of inorganically bound chlorine (ICl), samples and standards were injected directly into the measuring cell of the chlorine detector. During this process, the flow of measurement gas from the oven into the cell was interrupted. To minimize changes in the concentration of acetic acid used in the electrolyte, an injection volume of 50 µL was selected for the sample and standards.

Method parameters for furnace measurements (TCl)

Table 1: Method parameters for TCl determination

Parameter	Setting
Furnace temperature	1,050 °C
Second combustion phase	180 s
Ar flow (first phase)	100 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	100 mL/min

Process parameters for the coulometric cell

The following settings were established for the coulometric measuring cell and used for both the TCl and ICl measurements, in which the sample was injected directly into the measuring cell.

Table 2: Process parameters multi EA 5100 Cl

Parameter	Setting
Max. integration time	1.200 s
Cell temperature	23 °C
Titration delay	1 x 30 s
Threshold	300 cts
Threshold value	25 cts
Baseline/drift correction	Automatic
Maximum Drift	100 cts/min
Variation coefficient	3%

Results and discussion

Before the actual sample analysis, control standards were used to verify that the selected method settings and the calibrations performed provided sufficient stability for routine measurements. To this end, control standard A, which consists of organically and inorganically bound chlorine (c_{OCl} = 6.9 mg/L and c_{ICl} = 5.7 mg/L) and has a TCl content of 12.6 mg/L, was analyzed both by combustion (-> TCl) and by direct injection into the coulometric cell (-> ICl). Ten measurements were performed in each case.

In the next step, control standard B, which contained only inorganically bound chlorine (c_{ICl} = 10 mg/L), was analyzed in the same manner as control standard A. Here, too, 10 replicate measurements were performed.
After excluding outliers, eight measurements were used to calculate the performance parameters. The measurement series concluded with the analysis of an ethanol sample. All measurement results are summarized in table 3.

Table 3: Results TCl and ICl measurements for samples and control standard

Sample ID	Result TCl ± SD [mg/L]	RSD [%]	Recovery Rate [%]	Result ICl ± SD [mg/L]	RSD [%]	Recovery rate [%]
Control standard A n = 8/10	12.5 ± 0.22	1.8	99	5.3	4.5	94
Control standard B n = 8/10	10.2 ± 0.33	3.2	102	10.1	2.7	101
Ethanol sample n = 2	2.29 ± 0.10	4.6	–	0.80 ± 0	1.2	–

The following conclusions can be drawn from the results obtained for control standards A and B:
The recovery rate for control standard A was 99% for the TCl content and 94% for the ICl content. This confirms that both chlorine species are completely released during the combustion process and that the determination of the inorganic chlorine content via direct cell measurement is not influenced by the organic chlorine content. This finding is also confirmed by the very good reproducibility observed for both multiple determinations. RSD values of < 2% were achieved for TCl, and RSD < 5% for ICl.

Similar conclusions can be drawn for control standard B (inorganically bound chlorine only). The recovery rates here were 102% for the TCl content and 101% for the ICl content. Here, too, very good reproducibility was achieved across the eight replicate measurements: 3.2% RSD for TCl and 2.7% RSD for ICl. From this, it can be concluded that all inorganically bound chlorine is converted into the target analyte during combustion. Furthermore, the coulometric measuring cell, including the electrolyte, remains stable over a long period of time, even though the volume of the electrolyte changes due to the repeated injections and the acetic acid is thus diluted.

Based on the excellent results for the control standards, it can be expected that reliable results for TCl and ICl can be obtained very quickly for real samples. This was confirmed by the measurements of the ethanol sample. The correspsonding measurement curves are shown in table 4.

Table 4: Example measurement curves TCl and ICl

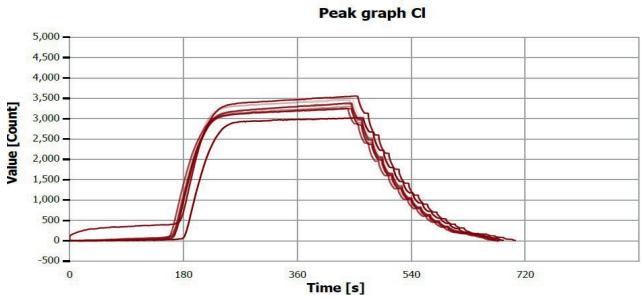
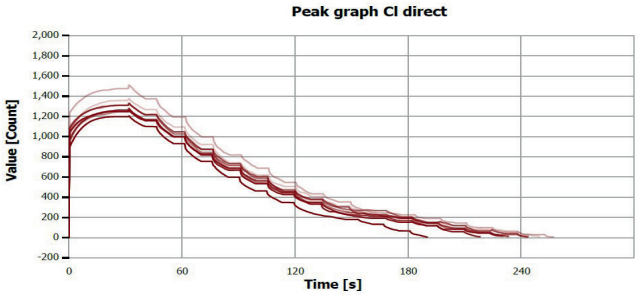
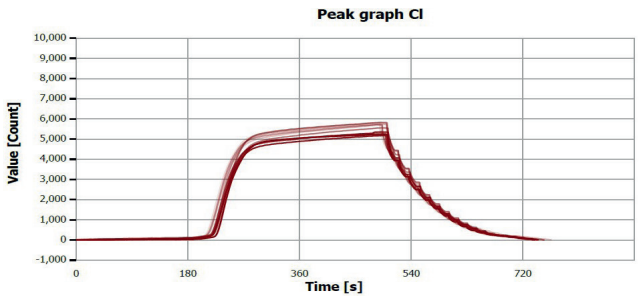
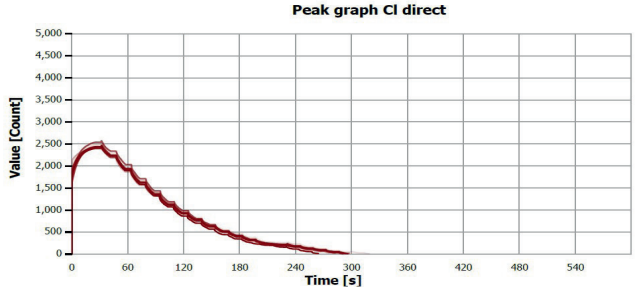
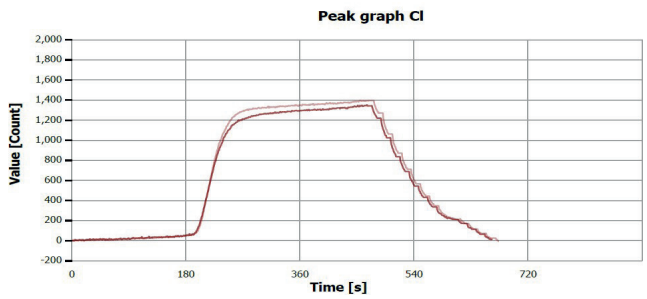
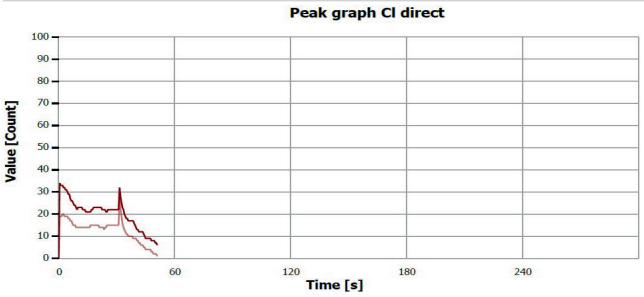
Measurement curves TCl	Measurement curves ICl
 Control standard A - combustion	 Control standard A – cell direct
 Control standard B - combustion	 Control standard B – cell direct

Table 4 (continued): Example measurement curves TCl and ICl

Measurement curves TCl	Measurement curves ICl
	
Ethanol sample - combustion	Ethanol sample – cell direct

Summary

The multi EA 5100 Cl, in combination with the high sensitive cell, offers a fast and reliable solution for the precise determination of inorganically bound chlorine and total chlorine in ethanol and related matrices. Thanks to the optimized digestion process and the associated quantitative conversion, excellent results are achieved regardless of the ratio of chlorine species present in the sample. The micro-coulometric measurement system, including the high sensitive cell, exhibits high stability during the direct injection of ethanol samples. The results for the direct determination of the inorganic chlorine content remain unaffected by organic chlorine compounds that may also be present in the sample. Furthermore, this method of ICl determination is very fast and simple.

High sample throughput can be easily achieved by using an MMS autosampler equipped with 112 position liquids kit. For lower throughput requirements, semi-automatic sample introduction via an autoinjector is an alternative.
If necessary, the modular multi EA 5100 analysis system can be expanded at any time by upgrading it with additional detectors or sample supply systems for the analysis of other elements (e.g., nitrogen, sulfur, carbon), sample types (gases/LPG, solids) or for sample preparation according to pyrohydrolysis for halide speciation, such as fluorine.

Figure 3: multi EA 5100

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
multi EA 5100 basic unit	450-300.011	multi EA 5100 combustion elemental analyzer for the determination of sulfur, nitrogen, chlorine, and carbon in solids, liquids, and gases
Cl module 5100	450-300.023	Extension of the multi EA 5100 for chlorine determina-tion by coulometric titration
Extension kit Cl high sensitive	450-300.024	Extension of the multi EA 5100 chlorine module for the determination of very low chlorine concentrations
Autoinjector - type AI-EA	450-900.461	Sample supply module for semi-automated injection of liquids
multiWin software	450-011.803	Control and evaluation software for multi EA 5100

Alternatively the autoinjector AI-EA could be replaced by the Multi Matrix Sampler MMS (450-300.030) equipped with liquids kit for MMS 5100 (450-300.033) to satisfy higher throughput demand or to enable more operational comfort.
Optionally, horizontal operation can be performed using an automatic boat drive (ABD) with flame sensor technology (450-300.013).

References

[1] ASTM D4929-24 Standard Test Method for Determination of Organic Chloride Content in Crude Oil

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