Standard Test Method for Determining Organic Chloride in Aromatic Hydrocarbons and Related Chemicals by Microcoulometry according to ASTM D5808

Challenge

Fast, sensitive and safe analysis of chlorine trace contents in different ultrapure aromatic and aliphatic hydrocarbons and their mixtures.

Solution

Optimized vertical combustion, gas purification by Auto-Protection system for effective prevention of condensation loss.

Introduction

Liquid hydrocarbons play an important role in refineries, the petrochemical, chemical and polymer industries, either as raw materials, process intermediates, or as end products. Regardless of their origin or further use, they all have in common that they should be ultra-pure when it comes to chlorine ($c < 100$ µg/L). If present, chlorine compounds can damage equipment (e.g., hydrotreatment or refinery reactors, pipelines and storage tanks) by formation of corrosive hydrochloric acid through hydrolysis processes or chemical reactions. Chlorine compounds – no matter if organic or inorganic – negatively affect the production process and the quality of the end products by formation of undesired by-products and catalyst poisoning. Since this happens even in presence of smallest traces, the maximum chlorine levels for process streams and final hydrocarbon products are defined in various standards. A stringent control with fast, reliable and highly sensitive analysis techniques is crucial to ensure adherence to those regulations.

The most effective method for a fast and reliable analysis is high-temperature combustion in combination with coulometric titration. The multi EA 5100 is an analysis system which has been specifically optimized for this challenging task. With its Auto-Protection system and highly sensitive detection, it allows the determination of chlorine traces as low as 50 µg/L.

Materials and Methods

Samples and Reagents

Different aliphatic and aromatic hydrocarbons and their mixes (e.g., isooctane, naphtha, etc.)

- Isooctane (C_8H_{18}), Suprasolv®, GR for gas chromatography (Merck Art.-No.: 1.15440.1000)
- 2,4,6-trichlorophenole ($C_6H_3Cl_3O$), GR for synthesis (Merck Art.-No.: 8.18469.0100)
- Standard kits for calibration and testing (Analytik Jena, Art.-No.: 402-889.071, 402-889.166)

Sample Preparation

The samples are light volatile, have a low viscosity, and contain TCl in the ultra-trace level. This made a pretreatment step redundant. The samples were analyzed directly.

Calibration

Prior to the actual determination, the system was calibrated using chlorine standard solutions based on 2,4,6-trichlorophenole (Cl) in isooctane. Figure 1 depicts a typical calibration curve and the performance parameters for ultra-trace applications.
The calibration was checked with different concentrated standards.

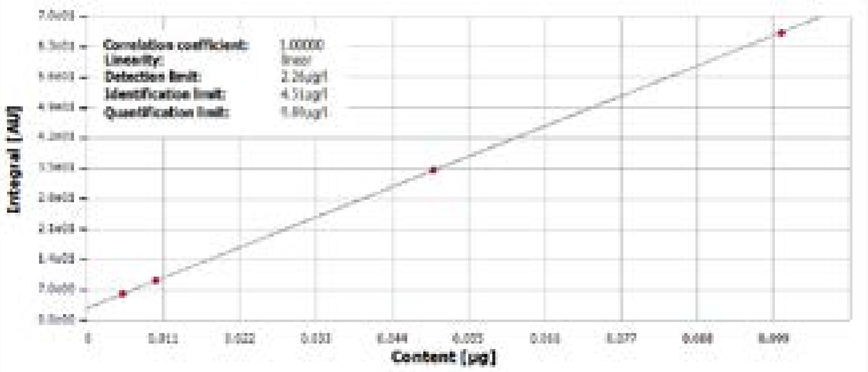

Figure 1: Example of a TCl calibration for the ultra-trace range, curve including statistics

Instrumentation

The measurements were performed using a multi EA 5100, equipped with Cl moduleand a high-sensitive chlorine cell for the determination of chlorine traces and ultra-traces. Sample introduction was carried out fully automatically to ensure maximum sample throughput.

The analyses have been run in vertical operation mode. The samples were dosed directly into the evaporation zone of the quartz glass combustion tube. This process took place fully automatically by means of the MMS multi matrix sampler in liquids mode. The catalyst-free, bi-phasic combustion process is carried out at temperatures of up to 1,050 °C. In the first process phase, evaporation of volatile sample components in an inert gas stream takes place, followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second phase the heavier, nonvolatile sample components and formed pyrolysis products are quantitatively oxidized in pure oxygen. This establishes the best conditions for a reproducible and fast ultra-trace analysis. The implemented Auto-Protection system (particle and aerosol trap) in combination with heated transfer lines guarantees highest operational safety and a complete transfer of the formed hydrogen chloride into the titration cell without adsorption or condensation losses. The multi EA 5100 enables a detection limit as low as 50 µg/L Cl.

Figure 2: multi EA 5100 with MMS in vertical operation mode

Method Parameters

The standard method ASTM D5808 from the method library of the analyzer's multiWin software was used for all analyses. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters multi EA 5100

Parameter	Specification
Operation mode	vertical
Furnace temperature	1,050 °C
Second combustion	60 s
Ar flow (first phase)	100 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	100 mL/min
Draw up	2 µL/s
Injection volume	100 µL
Injection	0.5 µL/s

Evaluation Parameters

Standard method settings were applied. The parameter settings are summarized in the following table.

Table 2: Detection parameters for the high sensitive cell

Parameter	Specification
Max. integration time	600 s
Threshold value	300 cts
Max. drift	100 cts/s
Cell temperature	23 °C
Titration delay	30 s
Threshold	25 cts

Results and Discussion

The examined samples are a representative spectrum of hydrocarbons from refinery applications, the petrochemical and chemical industry. The results given in Table 3 are averages of three replicate analyses of samples and test standards. Figures 3–6 show typical measuring curves for selected samples resp. standards.

Table 3: Results of the total chlorine determination in different samples and standards

Measurement	TCl	SD
Isooctane	47.5 µg/L	± 0.33 µg/L
Naphtha	1.40 mg/L	± 0.02 mg/L
Xylene	29.9 µg/L	± 1.03 µg/L
TCl Standard (c = 100 µg/L)	101 µg/L	± 3.82 µg/L
TCl Standard (c = 1.00 mg/L)	0.99 mg/L	± 0.01 mg/L

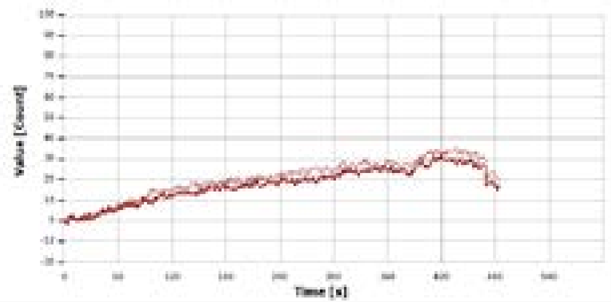

Figure 3: Analysis curve of “xylene”

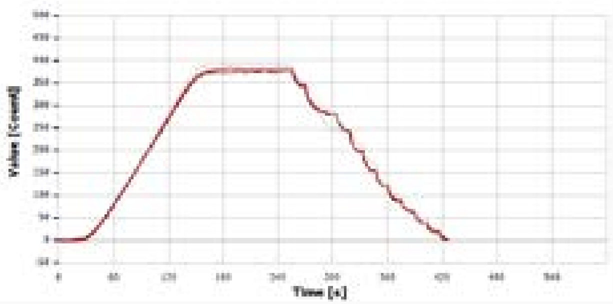

Figure 4: Analysis curve of “naphtha”

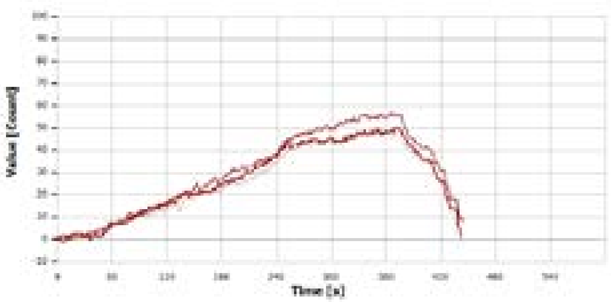

Figure 5: Analysis curve of “Cl standard 100 µg/L”

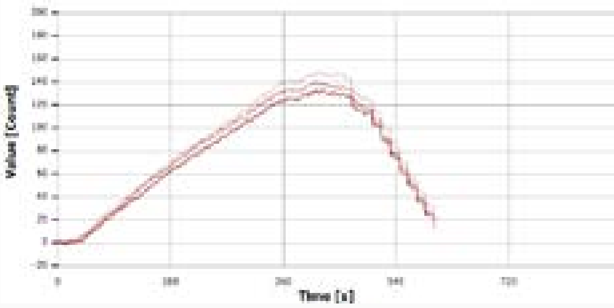

Figure 6: Analysis curve of “Cl standard 1 mg/L”

Due to the optimal process conditions a three- to fivefold determination, with injection volumes of 100 µL per replicate analysis, is sufficient to reach satisfying results for ultra-trace applications. This is remarkably affecting the sample processing time, generating a higher sample throughput. Utilization of large injection volumes and time-consuming strategies like trap-and-release are redundant. The analysis results received and their reproducibility depict the high quality of the sample combustion. The proper performance of the analysis system was confirmed by analyzing standard materials with known chlorine contents (see Table 3).

Conclusion

The multi EA 5100 is very well suited for the measurement of ultra-trace chlorine concentrations in versatile aliphatic and aromatic hydrocarbons and their mixes (e.g., naphtha, toluene, xylene, acetone). The detector, with its unique HiPerSens technology, achieves a measuring range of up to 100,000 mg/L starting at a limit of detection as low as 50 µg/L of chlorine.

The optimal sample digestion and the efficient Auto-Protection system, including a high-capacity dryer, enable excellent reproducibility, independent of the chlorine concentration or digestion characteristics and composition of the sample matrix analyzed. A high sample throughput is easily achieved by using the MMS liquids sampler. For lower throughput demands an autoinjector can be used alternatively.

If required, the analyzer can be easily extended to include the analysis of solids and gases by adding a matrix-optimized sampling system. For determination of nitrogen, carbon or sulfur contents one of the optional detection modules can be added as well.

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