Challenge

Automated, fast and trouble-free analysis of liquid samples of widely varying viscosities and Cl contents. Avoidance of sample pretreatment for high concentrations.

Solution

Fast, controlled horizontal combustion with flame sensor technology. Direct detection of Cl contents up to 10.000 mg/kg with sensitive cell option.

Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry according to IP 9076 resp. UOP 9076

Introduction

New petroleum products have to be tested for their chlorine content to ensure a sufficient product quality. Only this way undesired effects like corrosion and wearing of system components like engines, combustion and exhaust systems, tanks and nozzles, can be avoided when they are used as fuels (e.g., kerosene), combustibles for heating and power generation (e.g., diesel oil), or engine, lubricating or crankcase oil. That's why the chlorine contents generally are very low for new products. In contrast, used oils (e.g., transformer oil, vegetable oil) can be heavily contaminated with chlorine compounds due to their use. The chlorine content can vary from few ppm up to the wt% range. As a precondition for disposal and recycling of organic waste oils and related matrices the chlorine content has to be determined. Especially when being utilized as refused derived fuels (power generation, etc.), these matrices have to be strictly controlled to avoid not only exceedance of permissible emission limits (HCl), but also damages of the combustion system. Chlorine contents higher than 1 wt% significantly contribute to the formation and precipitation of alkaline and other metal chlorides at the colder installation parts like heat exchangers. This negatively affects performance, maintenance cycles, and finally, the economic life of these components.

In contrast to the classic methods – bomb digestion, Schöninger or Wickbold combustion – the combination of oxidative combustion with microcoulometric detection allows more flexibility, faster sample processing, as well as matrix- and content-independent quality of chlorine results.

The precondition for this method is the complete separation of the chlorine from the original sample matrix. This is more or less difficult, depending on the complexity of the sample composition. Especially long-chained, unsaturated, branched and cyclic compounds tend to vigorous digestion (spilling, smoldering, pyrolysis) when being heated up. In case of such an incomplete combustion, the chlorine recovery also is affected. This is due to the fact that the formed soot (mainly elemental carbon and other highly condensed carbon compounds) tend to adsorb the generated hydrochloric acid. This is comparable to the adsorption on charcoals for AOX sample preparation and is even worse in case the contamination and residues are located at cold parts of the analysis system.

The multi EA 5100 offers a quick and reliable analytical solution. Its flame sensor technology effectively prevents incomplete combustion. This and intelligent performance-enhancing features, such as the auto-zero and the automatic drift control, ensure a stable system performance, independent of the chlorine content of the analyzed matrices. The used microcoulometric “sensitive“ cell option is able to determine chlorine quantities as low as 100 ng up to 100 µg. This way a unique wide concentration range can be covered with one and the same analysis method. A sample dilution is not necessary thanks to the unique wide operation range of the sensitive cell option.

Materials and Methods

Samples and Reagents

Different petroleum-based and synthetic organic oils, new and used, were analyzed.

- 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)
- Chlorine standard kits for calibration and test (Analytik Jena, 402-889.166, 402-889.163)

Sample Preparation

The samples were analyzed directly without dilution.

Calibration / Recovery Check

Liquid standards based on 2,4,6 trichlorophenole (Cl) in isooctane were used to check the system performance and recovery in the range of the expected chlorine contents. The determined recovery factor can also be used to correct/adapt analysis results.

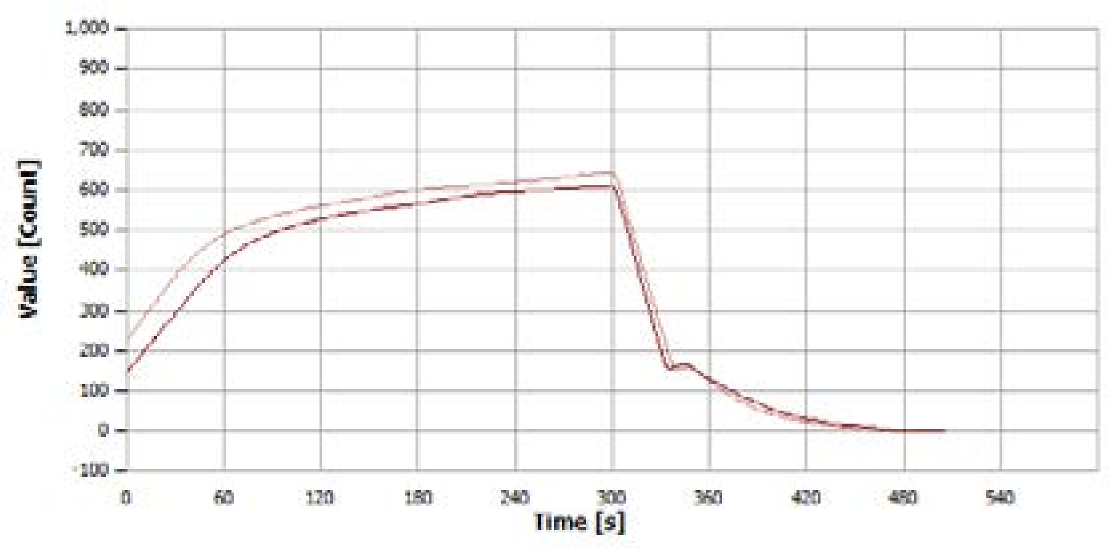

Figure 1: Example curve for a check standard analysis, 354.5 mg/L Cl

Instrumentation

The measurements were performed using a horizontally configured multi EA 5100, equipped with Cl module and extension kit „sensitive". Sample introduction was carried out fully automatically using the MMS multi matrix sampler with liquids kit (100 µL syringe) in combination with the ABD, an automatic boat drive with cooled sample introduction zone. This ensures a high sample throughput and best analysis results, even for samples with higher viscosity or complex composition. The analyses have been run in horizontal operation mode. Therefore the samples were dosed directly by means of the MMS in the liquids mode into a quartz sample boat which was placed inside the automatic boat drive. A special wide-bore needle allows to precisely draw-up and to dose even oils with a high viscosity without bubble formation. The used sample boat is filled with a sufficient amount of a sacrificial material. This is used to reduce effects of inorganic contaminants. After sample injection the ABD is fully automatically transferring the loaded boat into the hot zone of the combustion tube. This process is controlled and optimized by the flame sensor technology.

Sample digestion is carried out by a catalyst-free, bi-phasic process at temperatures of up to 1,050 °C. In the first process phase, evaporation of volatile and pyrolysis of the heavier sample components takes place in an inert gas stream. This is followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second phase the heavier, nonvolatile sample components resp. formed pyrolysis products are quantitatively oxidized in pure oxygen. Thereby the flame sensor technology ensures a uniform evaporation and quantitative combustion for any component of the sample matrix. Incomplete combustion, system contamination and thereby caused, low quality of analysis results (too low, scattering) is prevented effectively. This establishes the best conditions for analysis of any matrix type, even for diesel oil, vacuum gas oil, hydraulic fluids, or engine oil, independent of the introduced sample quantity. The horizontal mode is especially recommended for challenging or unknown samples with high element contents, vigorously reacting or inhomogeneous materials. Of course the horizontal mode is also suited for any other easy-to-process sample with lower element contents. The implemented Auto-Protection system guarantees highest operational safety, including a particle and aerosol trap. The powerful heating function for gas transfer lines helps to prevent undesired condensation and absorption loss for the formed hydrochloric acid, a precondition when chlorine has to be precisely determined. After drying by means of concentrated sulfuric acid, the formed hydrochloric acid gas is transferred to the titration cell, where it is absorbed in the acetic acid-based high-capacity electrolyte. After completed accumulation, the chlorine content is determined by means of a coulometric titration.

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

Method Parameters

The method *TCl_s_hori_liquid* from the method library of multi EA 5100 was used for all measurements. It is suitable for analysis of liquids, also for those with a high viscosity, or boiling points above 400 °C. Here only the horizontal mode can ensure reliable analysis results in the shortest possible time without maintenance increase. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters multi EA 5100 in horizontal mode with flame sensor technology

Parameter	Specification
Furnace temperature	1,050 °C
Cooling time (boat)	240 s
Second combustion	60 s
Ar flow (first phase)	200 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	200 mL/min
Draw up	2 µL/s
Injection volume	50 µL and 100 µL
Injection	3 µL/s

Evaluation Parameters

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

Table 2: Detection parameters for the sensitive cell

Parameter	Specification
Max. integration time	600 s
Cell temperature	18 °C
Titration delay	30 s

Results and Discussion

The analyzed samples are different petroleum products. The results given in Table 3 are averages of three replicate analyses of samples and one test standard. For all samples and standards injection volumes between 50 µL and 100 µL were used.

Table 3: Results of the total chlorine determination in different oil matrices and standard solutions

Measurement	TCl	SD
Used oil mix	719 mg/L	± 2.97 mg/L
Transmission oil	38.6 mg/L	± 2.18 mg/L
Engine oil	18.6 mg/L	± 0.47 mg/L
Waste oil	2,140 mg/L	± 16.2 mg/L
Transformer oil	23.4 mg/L	± 0.23 mg/L
Test standard Cl = 10 mg/l	10.1 mg/L	± 1.67 mg/L
Test standard Cl = 1,000 mg/l	1,000 mg/L	± 0.56 mg/L

Figures 3-5 show typical measuring curves for selected samples resp. standards.

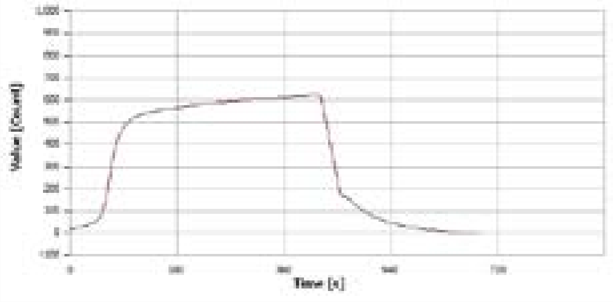

Figure 3: Analysis curve of “used oil mix”

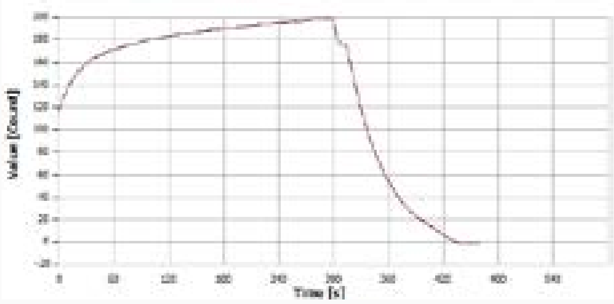

Figure 4: Analysis curve of “transformer oil”

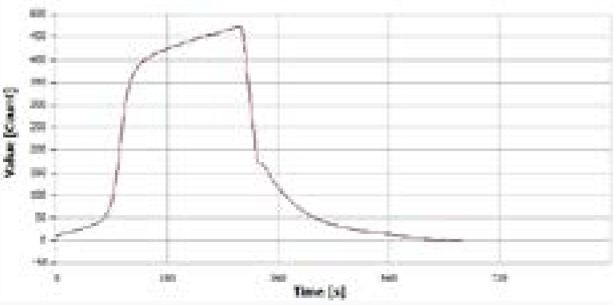

Figure 5: Analysis curve of “TCl standard 1,000 mg/L””

Due to the matrix-optimized combustion, in general a threefold determination is sufficient to achieve results far below 3% RSD. This remarkably affects the sample processing time and allows a higher sample throughput. The analysis results received and their reproducibility prove the performance of the digestion process. The overall performance of the analysis system was validated by analyzing standard materials with known chlorine contents, results are given in Table 3.

Conclusion

The multi EA 5100 with the sensitive cell option provides a fast and reliable solution for the precise determination of widely varying chlorine contents, even in the most challenging sample. Thanks to the fully automatically optimized digestion process and the quantitative conversion, best results can be achieved for any matrix in the shortest possible time, independent of its properties. This simplifies daily routine work and helps to increase sample throughput remarkably while operation effort and maintenance need is reduced.

The optimal sample digestion, the efficient Auto-Protection system and a heating of relevant transfer parts enable excellent reproducibility of results. A high sample throughput is easily achieved by using the MMS in liquids configuration with 112 position rack. For lower throughput demands manual introduction of the samples by means of boat injection (ABD) is possible alternatively.

If needed, the analysis system can be extended for the analysis of other matrix types like gases and solids, or the determination of additional elements and parameters (e.g., nitrogen, sulfur, carbon, TOC, AOX, EOX) by just adding the suited sampling or detection system.

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.

Headquarters
Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.0 | Author: AnGr
en · 12/2020

© Analytik Jena GmbH | Pictures (p. 1) ©: Shutterstock/Africa Studio