Challenge
Fast and trouble-free analysis of liquid samples with a high amount of phosphorus-organic compounds. Prevention of system damage and formation of phosphorus oxides/acids.

Solution
Controlled horizontal combustion with boat inlet. Effective gas purification and prevention of absorption and condensation for high detection sensitivity.

Intended audience
Analytical laboratories, industrial users with hydraulic systems, fluid manufacturers and service/maintenance providers.

Determination of total chlorine in different types of hydraulic fluids by coulometric titration after high-temperature combustion

Introduction

Hydraulic fluids are used in different technical equipment and machines such as steering systems, brakes, versatile transmissions, aircraft flight control systems, wind engines, excavators, etc. Depending on the purpose of use and the desired properties (e.g., biodegradable, anti-wearing, fire-resistant), a wide variety of different types of hydraulic fluids is available. They are either organic, based on mineral or vegetable oil, or synthetic, e.g., based on silicone or phosphate esters.

A major disadvantage of hydraulic fluids such as mineral oil-based ones is that they are flammable. This can cause serious consequences in case of an incident, especially when used in aircrafts, where immediate fire-fighting measures during a flight are nearly impossible. That is why fire-proof products are used for airplanes. The best known representative of this class is SkydrolTM, a synthetic, phosphate ester-based formulation.

To avoid dangerous situations caused by corrosion or too early degradation of the hydraulic system and fluid, quality, composition and wearing degree of the fluid have to be regularly monitored. Besides the main parameters such as acidity, presence of water and particles, the concentration of the elements calcium, sodium, potassium, sulfur, and chlorine also has to be checked.

Chlorine is not part of the composition of such high-performance hydraulic fluids. Nevertheless it can be included due to contamination effects, e.g. when cleaning the hydraulic systems with chlorinated solvents. In case the system is not completely dried before refilling with the hydraulic fluid, contaminations are easily possible. The maximum permissible value of 200 ppm must not be exceeded.

analytikjena
An Endress+Hauser Company

Chlorine determination in greases and other oil-based formulations (e.g., crude oil, transformer oil, engine oil) is not a big challenge due to the predictable digestion behavior of these matrices. But when it comes to high-performance hydraulic fluids like SkydrolTM, the case is completely different. Due to the matrix itself – mainly organic phosphate esters – it is not only highly fire-resistant, but also leads to the formation of large amounts of particles such as P4O10, during the combustion process. Even worse, these particles react with the formed combustion water by immediate hydrolysis to i.e. H3PO4. Measuring chlorine sensitively and reliably under such conditions without damaging the analysis system is extremely challenging.

The multi EA 5100 with its powerful Auto-Protection system effectively protects the analysis system by trapping all particles, aerosols and the liquid acid, while the formed hydrochloric acid can pass through easily thanks to the integrated heating. The analyzer's high sensitive coulometer cell is able to determine chlorine quantities as low as 10 ng up to 10 µg. This way a wide concentration range can be covered with one and the same analysis method. A sample dilution is not necessary.

Materials and methods

Samples and reagents

Different hydraulic fluid samples (different SkydrolTM types) have been 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)
- Standard kits for calibration and test (Analytik Jena, Art.-No.: 402-889.071, 402-889.166)

Sample preparation

The samples were analyzed directly without dilution due to the expected low chlorine contents.

Calibration

Liquid calibration standards based on 2,4,6 trichlorophenole (Cl) in isooctane were used to calibrate the analysis system in a wide concentration range. Matrix-related calibration strategies were not required as the combustion is optimized and interfering components are eliminated before detection. The calibration was checked with different concentrated standards.

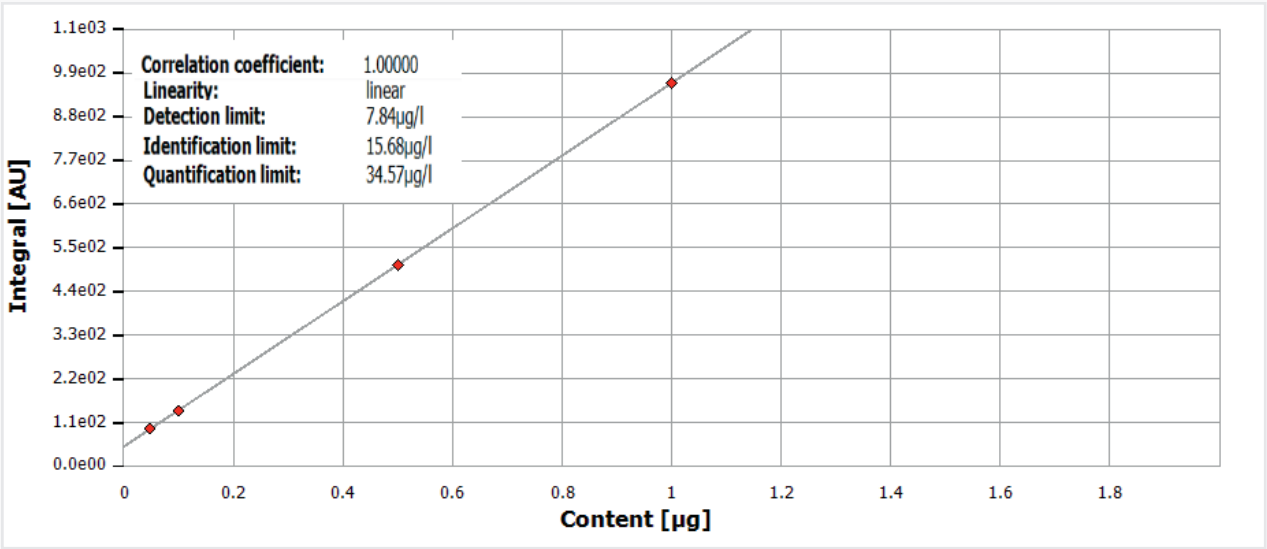

Figure 1: Exemplary calibration for TCl middle range, curve including statistics

Instrumentation

The measurements were performed using a horizontally configured multi EA 5100, equipped with a block-shaped Auto-Protection system and coulometric chlorine module with high sensitive cell. Sample introduction was carried out fully automatically using the MMS multi matrix sampler in liquids mode in combination with the ABD, an automatic boat drive with a 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. Using the MMS in liquids mode, the samples were dosed directly into a quartz sample boat which was placed inside the automatic boat drive. This boat is filled with a sufficient amount of a sacrificial material. This is used to reduce effects of the phosphorus compounds, which are main components of the sample matrix. After sample injection the ABD is fully automatically transferring the loaded boat into the hot zone of the combustion tube.

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. 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 effectively prevented. This establishes the best conditions for analysis of any matrix type, even for untreated vacuum gas oil, hydraulic fluids, light naphtha, or crude oil, independent of the introduced sample quantity. The horizontal operation mode is especially recommendable for challenging or unknown sample matrices with high element contents, vigorously reacting or inhomogeneous materials. Of course the horizontal mode is just as well suited for any other easy-to-digest sample with lower element contents. The implemented Auto-Protection system guarantees highest operational safety, including a particle and aerosol trap, which captures the formed phosphorus oxides and acids before they can harm system components, clog gas paths or affect the chlorine detection. The powerful heating function for the gas transfer line helps to prevent undesired condensation and absorption loss for the formed hydrochloric acid. This is a precondition when chlorine ultra-traces have to be determined precisely. After drying, 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 coulometric titration. The multi EA 5100 enables a detection limit of as low as 50 µg/L Cl.

Method parameters

The method TCl_hs_hori_liquid from the method library was used for all measurements.

It is suited for analysis of liquids, also for those with high viscosity, or boiling points above 400 °C. Here only the horizontal mode can ensure reliable analysis results in the shortest possible time without increasing maintenance efforts. To allow for a higher processing speed for samples which are too viscose for introduction by syringe, the syringeability can be enabled by a sufficient dilution with a suitable solvent (e.g., xylene), alternatively a wide-bore needle can be used. Table 1 on the following page 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
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 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 analyzed samples are different hydraulic fluids. The results given in Table 3 are averages of three replicate analyses of samples and one test standard. For all samples and standards an injection volume of 50 µL was used.

Table 3: Results of the total chlorine determination in different hydraulic fluids and one standard

Measurement	TCl	SD
Hydraulic fluid 1	8.67 mg/L	± 0.20 mg/L
Hydraulic fluid 2	17.9 mg/L	± 0.08 mg/L
Hydraulic fluid 3	10.4 mg/L	± 0.30 mg/L
Hydraulic fluid 4	11.9 mg/L	± 0.08 mg/L
Hydraulic fluid 5	12.7 mg/L	± 0.36 mg/L
Test standard Cl = 10 mg/L	9.95 mg/L	< 0.01 mg/L

Figures 3–6 show typical measuring curves for selected samples and the standard.

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 a standard material with known chlorine content, results are given in Table 3.

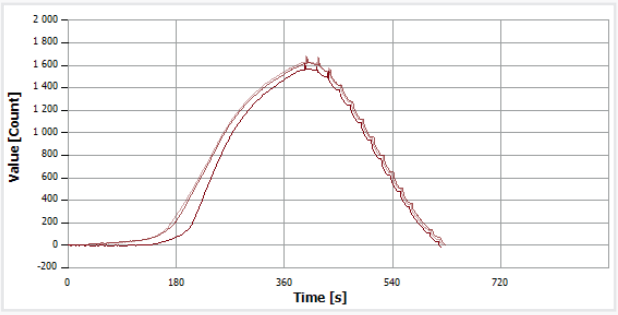

Figure 3: Analysis curves of "Hydraulic fluid 1"

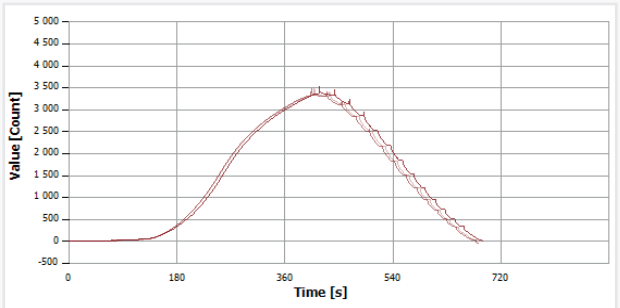

Figure 4: Analysis curves of "Hydraulic fluid 2"

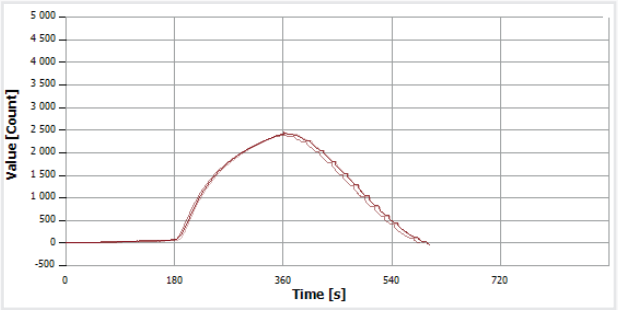

Figure 5: Analysis curve of "TCl standard 10 mg/L"

Summary

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

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

Figure 6: multi EA 5100 with ABS and MMS

Recommended device configuration

Table 4: Overview of devices, accessories, and consumables

Article	Article number	Description
multi EA 5100	450-300.011	Elemental analyzer for determination of sulfur, nitrogen, carbon
Cl module	450-300.023	Extension for chlorine determination by coulometric titration
Extension kit Cl high sensitive	450-300.024	Extension kit high sensitive for Cl module
Automatic Boat Drive - ABD	450-300.013	Flame sensor controlled sample supply in horizontal mode
MMS – Multi Matrix sampler	450-300.030	Autosampler for liquids and solids
Liquids kit for MMS	450-300.033	Extension kit for MMS for dosing of liquids
multiWin software	450-011.803	Control and evaluation software, incl. method library
Auto-Protection assembly for AOX	402-889.528	AP system especially for Cl analysis systems

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.
Trademark notice: The brand names of the third-party products specified in the application note are usually registered trademarks of the respective companies or organizations.

Headquarters
Analytik Jena GmbH+Co. KG
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 1.2 · Author: AnGr
en · 06/2026
© Analytik Jena GmbH+Co. KG |
Picture p. 1 ©: Shutterstock/Hanna Kuprevich