



Challenge

Easy fully automated, sensitive, and reproducible determination of chlorine ultra traces in highly viscous liquid glycerol samples

Solution

Highly sensitive coulometric detection after flame sensor-controlled quantitative combustion of slightly diluted glycerol samples

Intended audience

Industrial quality control labs; producers of oleochemicals, base chemicals, biochemicals, biofuels; petrochemical industry, production of skin care and cosmetic products, contract labs

Determination of Widely Varying Chlorine Contents in Glycerol and MCT Oil by Combustion Elemental Analysis with Coulometric Titration

Introduction

Sustainable alternatives to mineral oil-based fuels gain more and more importance to reduce the CO₂ footprint, but also to cover the gap when fossil feedstocks become scarce. One of them is the classic biodiesel also known as FAME (fatty acid methyl ester), which is either used directly or as a blend component in various ratios (e.g., B5, B10) for diesel fuel. Feedstocks for production of FAME can be very versatile. Vegetable oils like rapeseed, soy or palm oil, or waste materials like used cooking oil or even animal fat (tallow) from abattoir refuse are used most frequently. But independent of feedstock origin, at the end they all contain triglycerides. A triglyceride is an organic ester consisting of three linear, unsaturated fatty acids bound together to one glycerol molecule. To produce FAME, these bonds must be broken ahead of esterification of the free fatty acids with methanol. This process is well known as catalytic transesterification. Besides FAME, glycerol (propan-1,2,3-triol) appears as a byproduct in a considerable yield.

Besides other intermediate products such as mono-, di-, and triacyl-glycerides as unmodified feedstock, which are not of relevance, the remaining free methanol and the catalyst (NaOH, KOH, or alkoxides) can be reused after purification. Besides biofuel production, glycerol is also a byproduct of saponification of vegetable oil or can be directly produced in the petrochemical industry based on propene. Glycerol, also known as glycerin, is an alcohol, a so called triol. Due to its positive properties, it has many industrial applications and can be used as humectant, preservative, emulsifier, softener, or lubricant. Glycerol is used as base material, ingredient, or additive in cosmetics (lotion, make-up), pharmaceuticals (suppositories, vaccines, pain reliever), and the food industry (ice cream, bakery products, electric cigarette liquids), or other industrial products like resins and protective coatings, or even explosives (nitroglycerin). Glycerol can also be a feedstock for the chemical industry, e.g. for the production of hydrogen (catalytic reforming)

or other chemicals (trifunctional polyether polyols, isopropylidene glycerol).

But for these uses, only pure, high-quality glycerol can be used. This requires sufficient cleaning and purification, e.g., by distillation. To meet the quality requirements, glycerol must be free of dangerous impurities like organic chlorine compounds. These could have enriched in the glycerol during FAME production from processing or the feedstock materials itself. To ensure this, a robust and highly sensitive matrix-independent analysis technique is needed. While XRF is well suited for higher chlorine contents (ppm-%), like in crude oil and used mineral oils, this technique is not able to deliver results for the ultra-trace range (< 1 mg/L). For such a challenging task, combustion based elemental analysis coupled with coulometric titration has proven to be highly

sensitive, being able to detect chlorine contents as low as 50 µg/L. But still, combustion is a challenge that is able to falsify chlorine results. If combustion is not quantitative, soot and other pyrolysis residues are formed inside the analyzer. This impairs the transfer of the HX gas formed, which leads to low, arbitrary scattering results and significantly increased maintenance costs. Glycerol is not an easy matrix, due to its high viscosity, combustion behavior, and the partly inhomogeneous distribution of contaminants inside the glycerol. Thus, sample introduction and the combustion process have to be optimized to ensure correct results. This application note describes the strategy for a quick and fully automated determination of chlorine contents in a very wide range, from ultra-traces to contents in the upper ppm range, using the multi EA 5100 elemental analyzer.

Materials and Methods

Samples and reagents

- Three different glycerol (glycerin) samples, colorless, viscous liquids
- One MCT oil (medium-chain triglycerides) sample, slightly yellow, viscous liquid
- Kit calibration solutions, c: 0.1–10 mg/L Cl, (Analytik Jena GmbH+Co. KG, 402-889.071)
- Ethanol absolute (C₂H₅OH), Suprasolv[®], grade: for gas chromatography ECD/FID, (VWR, Merck, Art.-No.: 1.02371.1000), as solvent for dilution

Sample preparation

To enable easy automation and high producibility, the samples have been diluted slightly, 1 to 1 before analysis. Ethanol was used as diluent for the mass-based dilution. The low dilution ratio was used to ensure that the chlorine impurities are not diluted below the limit of detection, but enough to decrease viscosity to enable dosing by a microliter syringe.

Calibration

Prior to the measurements, the multi EA 5100 was calibrated for chlorine determination. Therefore, liquid standards were used and blank correction was applied, as required for analysis in the trace range. Details related to the calibration and its ranges are summarized in table 1. The gained calibration has been verified with a certified reference standard. 100 µL injections have been used for both, calibration and verification measurements. Figure 1 and 2 show exemplarily calibration curves for chlorine in the trace and ultra-trace range.

Table 1: Calibration parameters for chlorine

Parameter	Standard	Calibrated range, Cl absolute	Range
TCI	2,4,6-Trichlorophenol in isooctane	0.25–5.00 µg	trace
TCI	2,4,6-Trichlorophenol in isooctane	0.00–0.25 µg	ultra-trace

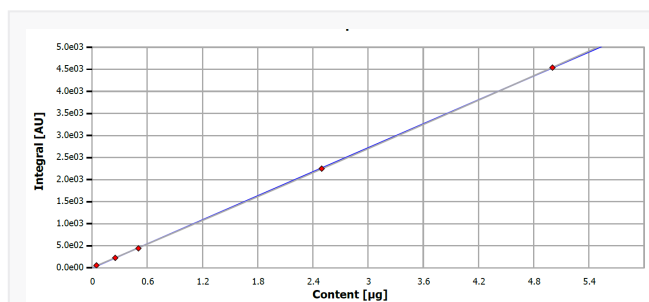


Figure 1: TCI calibration, trace range

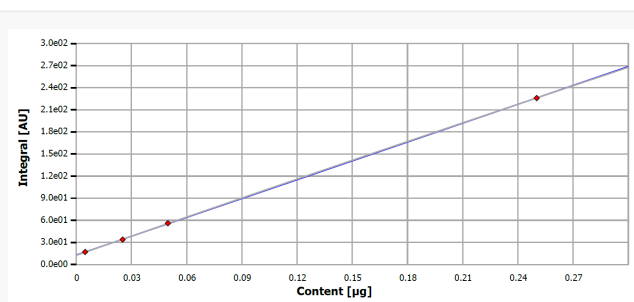


Figure 2: TCI calibration, ultra-trace range

Instrument settings

An elemental analyzer type multi EA 5100 was used in horizontal operation mode for the analysis of all sample dilutions and standards. For the determination of chlorine, coulometric titration using the high sensitive cell option was applied. The achievable detection limit of this measuring system is 50 µg/L Cl. For automated sample introduction and transfer into the combustion furnace, the system was equipped with an automatic boat drive (ABD) with flame sensor technology and a multi-matrix sampler (MMS). The flame sensor ensures safe and quantitative combustion of each sample matrix within the shortest possible measurement time. This eliminates the need for time-consuming method development and creation of boat programs for each sample type. This makes analysis simple and reproducible, eliminates sources of error, and reduces maintenance compared to classic boat programs.

For all the measurements, a defined volume of 100 µL was dosed into a quartz sample boat and placed in the automatic boat drive using the µL-syringe of the MMS. Afterwards, this boat was automatically transferred to the combustion furnace, controlled by the flame sensor. The flame sensor adapts the process to the special requirements of the

respective sample component, ensuring matrix-independent results.

Sample digestion was carried out by efficient catalyst-free high-temperature combustion. The process is divided into two phases. In the first phase, the volatile sample components are vaporized in an inert gas stream, followed by combustion of the gaseous products formed in an oxygen-rich atmosphere. In the second phase, the heavier, non-volatile sample components and the pyrolysis products formed are quantitatively oxidized in pure oxygen. The formed gaseous reaction products are dried and transferred to the detection systems. The contained HX gas is adsorbed completely in the electrolyte solution. The Auto-Protection system of multi EA 5100 guarantees highest operational safety and efficient protection, particles and aerosols are retained, only the analyte gas can pass.

Method parameters

A standard method from the method library of the multiWin software was used for the analysis of the standards and sample dilutions. The parameters for combustion and detection are summarized in Tables 2 and 3. The injection volume for the chlorine determination was 100 µL.

Table 2: Process parameters multi EA 5100 – horizontal mode

Parameter	Setting
Furnace temperature	1050 °C
2nd combustion	60 s
Ar flow (1st phase)	200 mL/min
O ₂ main flow	200 mL/min
O ₂ flow (2nd combustion)	200 mL/min
Sample: draw-up	2.0 µL/s
Sample: inject	2.0 µL/s
ABD module	automatic*

* Flame sensor controlled, automatically optimized combustion

Table 3: Detection parameters for Cl (high sensitive cell) detection

Parameter	Setting
Max. integration time	1200 s
Cell temperature	21 °C
Titration delay	1 (= 30 s)
Threshold	300 cts
Threshold value	25 cts
Baseline / drift correction	automatic

Results and Discussion

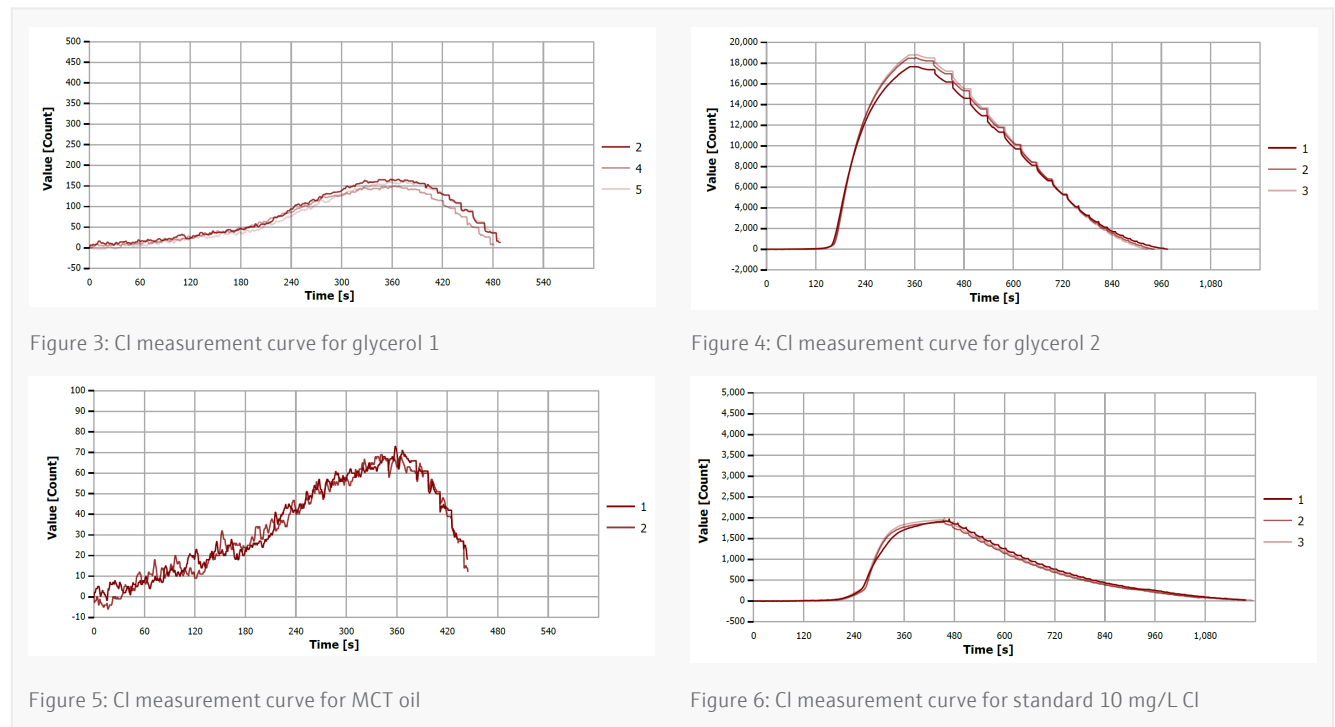
The results for the Cl determination of the control standards and different samples are summarized in Table 4. These are mean values from triplicate determinations. The high efficiency of combustion and sample introduction are reflected in the very good reproducibility and scattering below 3%. Even absolute chlorine quantities at the limit of detection as it is the case for the dilution of sample MCT oil (50 µg/L) show remarkably good RSD values. Such low concentrated samples could be analyzed direct without dilution as an alternative.

Table 4: Results of the TCI analyses for samples and standards

Sample	$c_{Cl} \pm SD$ [mg/L]	RSD [%]
Glycerol 1	0.37 ± 0.01	2.70
Glycerol 2	100 ± 2.49	2.50
MCT oil	0.12 ± 0.01	12.8
Standard 1.00 mg/L Cl*	1.05 ± 0.01	0.45
Standard 10.0 mg/L Cl*	10.0 ± 0.09	0.83

* measured undiluted

The figures 3 to 6 show representative Cl curves for one control standard and the samples.



Summary

The elemental analyzer multi EA 5100 offers a simple and reliable solution for precise and fast chlorine analysis in viscous liquids like polyols and fatty acids. The HiPerSens chlorine detection provides lowest detection limits and a very wide linear measuring range. This allows to analyze ultra-pure final products, feedstocks, and process intermediates in one single analysis cycle with the same analysis method, saving additional time.

The flame sensor enables reliable, reproducible, and fast digestion of any sample matrix without method development, thus guaranteeing exact results in the shortest possible measuring time. The formation of soot or other undesirable pyrolysis products and the resulting increased maintenance effort and incorrect analysis results are prevented from the outset.

If other analytical tasks come into focus, e.g., analysis of gases, solids, or the determination of additional elements like sulfur, nitrogen or carbon, the analyzer can be extended with suitable sample supply and detection systems at any time.



Figure 7: multi EA 5100 with ABD and MMS autosampler in liquids mode

Recommended device configuration

Table 5: Overview of devices and accessories

Article	Article number	Description
multi EA 5100	450-300.011	Basic module with combustion
Cl module 5100	450-300.023	Module for determination of chlorine contents by coulometric titration
Extension kit Cl "high sensitive"	450-300.024	Extension for chlorine determination in the trace range
Automatic Boat Drive - ABD	450-300.013	Automatic boat drive with flame sensor technology – sample supply in horizontal mode
Multi Matrix Sampler - MMS	450-300.030	Sampler for automatic dosing of liquids, solids, AOX, EOX and TOC samples
Liquids kit for MMS 5100	450-300.033	Accessory for the dosing of liquid samples
multiWin software	450-011.803	Control and data evaluation software

The configuration described above can also be used to analyze the undiluted samples, e.g., in solids mode.

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