



Challenge

Quick, concentration-independent direct sulfur determination for volatile samples in vertical mode

Solution

Optimized vertical combustion and efficient gas purification combined with HiPerSens UV-fluorescence detection (UVFD)

Intended audience

Industrial quality control labs, biofuel producers and blenders, producers of ethanol, methanol, and other alcohols, and contract labs

Determination of Sulfur in Methanol and Ethanol by Combustion Elemental Analysis with UV-Fluorescence Detection in Accordance with DIN EN 15486 and ASTM D5453

Introduction

Ethanol is primarily derived from sugar, starch, or ligno-celluloses through biochemical processes. Sugar can be directly fermented, while starch and celluloses require additional steps to break them down into smaller sugar molecules. Enzymatic hydrolysis is used to break down starch and celluloses into monosaccharides. Over the past decade, the production of ethanol has more than doubled due to increasing demand from the transportation sector. Adding sustainable fuels like bioethanol to fossil fuels is one of the quickest ways to reduce CO₂ emissions. Bioethanol is the synonym for ethanol used as a fuel or fuel additive. Different ratios of bioethanol are added to common fuels resulting in blends - E5, E10, E15, and E85. The number in the blend name indicates the percentage of alcohol added by volume. Most cars can use blends up to E10 without any modifications to their engines or fuel systems. However,

other vehicles require flexible fuel systems (FFV) to use higher ethanol blends. E100, pure bioethanol, can only be used by specifically manufactured engines. Initially, bioethanol was produced using sugars and starch from food crops, such as sugar beet and sugar cane. However, concerns arose about the competition for these feedstocks, which could lead to rising food prices and regional shortages. To address this issue, new feedstock materials and processes were developed using non-food sources such as biomass residue from agriculture, paper, or timber industries (e.g., nut shells, sawdust, and straw). While this approach reduced competition with food crops, it still occupied agricultural land. The development of third-generation biofuels helped to overcome this challenge by utilizing non-food materials cultivated in areas where traditional agriculture is not possible. For example,

microalgae, specifically engineered to maximize starch yield for bioethanol production, cultivated in specially designed reactors. These next-generation sustainable green fuels contribute to further reducing CO₂ emissions.

When ethanol is used as a fuel, it undergoes the same stringent controls for sulfur impurities like fossil fuels. It is important to remove sulfur during the production process of bioethanol, as sulfur compounds contribute to air pollution when used as a fuel blend component or in pure form. Like traditional fuels, bioethanol must adhere to strict sulfur content limits, such as 10 parts per million (ppm) in the European Union.

To ensure compliance with these limits, analysis standards and product specifications such as ASTM D4806, D5798, DIN EN 15376, and DIN EN 15293 are used. Bioethanol is generally a high purity additive with expected sulfur impurities below 1 ppm S. Therefore, a highly sensitive detection principle is required to measure sulfur concentrations of 1 ng S or less, without being affected by matrix effects caused by the high oxygen content of the sample.

Among all sulfur analysis techniques, combustion elemental analysis with UV-fluorescence detection is considered especially suited for bioethanol analysis. The most applied analysis norms for this technique are ASTM D5453, DIN EN ISO 20846, or DIN EN 15486.

Besides fuel production, ethanol can be used directly in many other ways, including food production, beverages, as an ingredient in pharmaceuticals, and as a disinfectant for health protection. In cosmetics it is used as carrier and solvent for creams, detergents, perfumes, and household products like antifreeze and cleaning agents, in paints and resin production. It is also used as a feedstock for the chemical industry to produce other chemicals like 2-ethoxy-2-methylpropane (ETBE), acetic acid (vinegar), ethene, ethyl acrylate, ethylene chloride, acetaldehyde, and many more. In the following, a method developed for the quick and reliable determination of sulfur ultra-trace impurities is described. This method was developed for pure alcohols like ethanol and methanol, but is also applicable 1:1 for fuel blends with different ratios of these alcohols and other matrices with high oxygen content (e.g., oxygenates).

Materials and Methods

Samples and reagents

- Two different grades of ethanol and three different grades of methanol
- Kit calibration solutions, c: 0.1–10 mg/L S, Analytik Jena GmbH+Co. KG, 402-889.070

Sample preparation

The samples and standards have been analyzed directly without sample pretreatment.

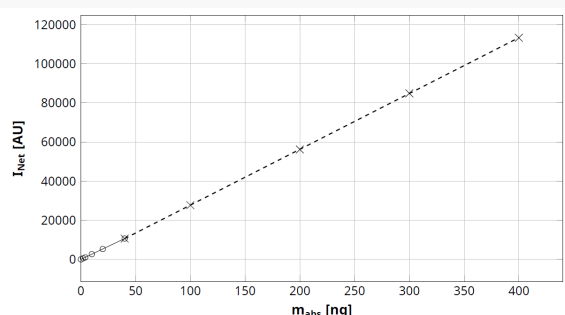


Figure 1: Calibration curve for sulfur

Calibration

Liquid calibration standards based on dibenzothiophene in isooctane were used to calibrate the analysis system before analysis. The resulting calibration curve is shown in figure 1. Table 2 shows the statistical data of both ranges. The quality of calibration was confirmed with different concentrated standard solutions of known concentration.

Table 1: Performance data of sulfur calibration

Parameter	Value
Injection volume	40 µL
Range	0-0.4 µg S absolute
Detection limit	4.72 µg/L S
Linearity	linear
Correlation coefficient	0.99996

Instrumentation

A combustion elemental analyzer type compEAct S was used for the analysis. Sample introduction was carried out by the liquids autosampler LS 2 to increase the sample throughput. 40 μL of the samples, and standard solutions were used for analysis. Sample digestion was carried out by efficient catalyst-free high temperature combustion in a quartz combustion tube, equipped with a quartz pyrolyzer. This ensures sharp peak modulation and thereby maximum sensitivity.

In the first process phase, evaporation of light components and pyrolysis of the heavier ones takes place within an inert argon atmosphere. The resulting gaseous products are converted in the pure oxygen atmosphere of the combustion zone. In the second phase the system switches completely to oxygen and the remaining components are combusted quantitatively. The implemented auto protection system guarantees highest operational safety, acting as a particle and aerosol trap, and ensuring complete transfer of the formed SO_2 into the HiPerSens UV-fluorescence detector. Thanks to its wide range, and ultra-low detection limit (LOD: 5 $\mu\text{g/L}$), even smallest sulfur contents can easily be quantified, no multiple injection, no huge sample volumes, nor trap and release approaches are required. The analysis of high element contents, up to 10.000 mg/L , is possible as well with the same method. Thus, concentration specific adaptation of the system or detector is not necessary, saving valuable operation time and material.

Method parameters

For analysis of the liquid standards and samples a standard library method was used. The process parameters are summarized in Table 2. The injection volume for the TS determination was set to 40 μL . The injection of standard and samples was done by means of the standard μL syringe. The same introduction parameters were used for both, no method adaptation in the software/hardware was necessary.

The evaluation parameters for the detection of sulfur contents by UV fluorescence are summarized in Table 3.

Table 2: Combustion parameters compEAct S

Parameter	Setting
Furnace temperature	1050 °C
2 nd combustion	60 s
Ar flow (1 st phase)	150 mL/min
O ₂ main flow	200 mL/min
O ₂ flow (2 nd phase)	150 mL/min
Draw up speed	2.0 $\mu\text{L/s}$
Injection speed	0.5 $\mu\text{L/s}$

Table 3: Detection parameters for total sulfur determination (UVFD)

Parameter	Setting
Max. integration time	360 s
Start	0.2 cts
Stop	0.5 cts

Results and Discussion

Three-fold analyses with outlier selection were done to check for repeatability of the injection and digestion process. The high repeatability is confirmed by the low RSD values. To ensure accuracy and reliability, two certified reference standards with known concentrations of sulfur were analyzed alongside the samples. All the results are summarized in Table 4.

Table 4: Results of TS determination for the samples and standard solutions

Sample	$c_s \pm SD$	RSD [%]
Methanol - 1	1.00 ± 0.01 mg/L	0.65
Methanol - 2	980 ± 4.70 μ g/L	0.48
Methanol - 3	950 ± 11.8 μ g/L	1.24
Ethanol - 1	2.20 ± 0.01 mg/L	0.34
Ethanol - 2	4.99 ± 0.06 mg/L	1.13
Standard, 1.0 mg/L S	990 ± 15.6 μ g/L	1.58
Standard, 5.0 mg/L S	5.07 ± 0.04 mg/L	0.80

Depending on the production approach and the feedstock quality, the sulfur content of the different alcohol batches varies slightly, as shown clearly by the ethanol results. In the following, exemplary measuring curves for samples and standards are depicted in figures 2 to 7.

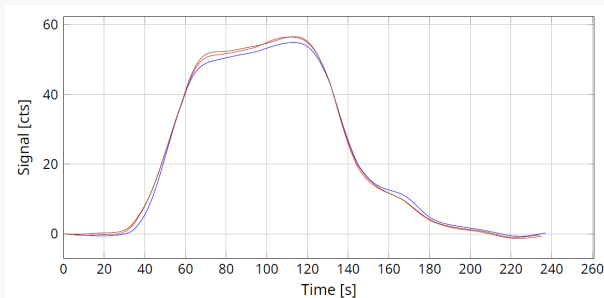


Figure 2: TS analysis curve of standard "1 mg/L S"

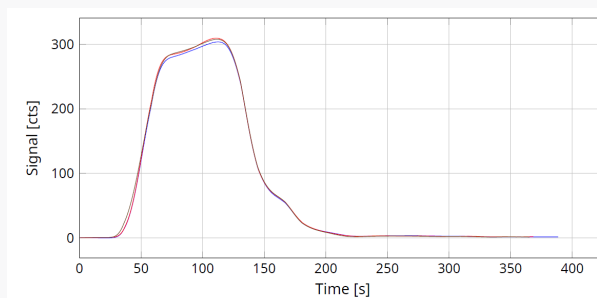


Figure 3: TS analysis curve of standard "5 mg/L S"

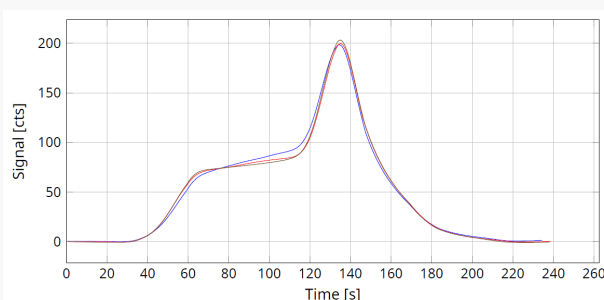


Figure 4: TS analysis curve of sample "Ethanol - 1"

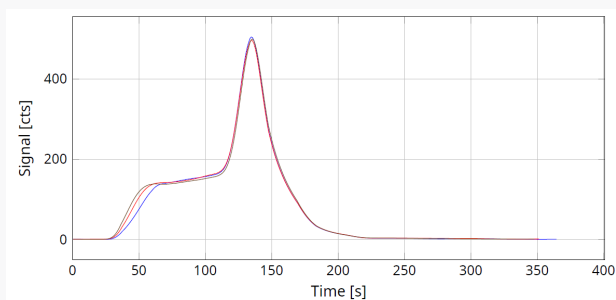


Figure 5: TS analysis curve of sample "Ethanol - 2"

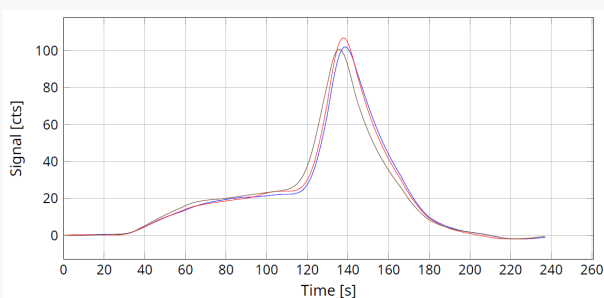


Figure 6: TS analysis curve of sample "Methanol - 1"

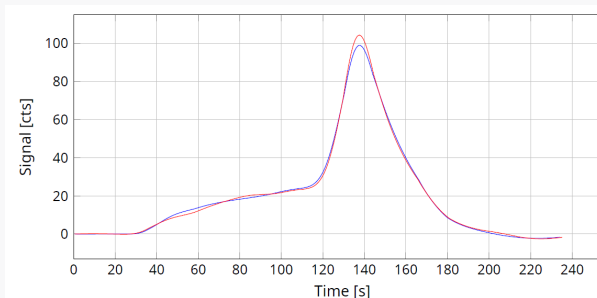


Figure 7: TS analysis curve of sample "Methanol - 2"

Summary

The total sulfur determination by combustion based elemental analysis with a UVFD detector has been used to get a quick measure for total sulfur content.

The compEAct S has proven suitable for this analysis task. It provides a fast and reliable solution for the precise determination of widely varying sulfur contents, even for challenging tasks like ultra-trace analysis in very light volatile hydrocarbons. A high sample throughput is easily achieved by using the LS 2, or alternatively the LS-T autosampler. The latter additionally offers a cooling option to prevent evaporation of very volatile samples.

Thanks to the HiPerSens technology, a measuring range starting as low as 5 µg/L of sulfur up to 10,000 mg/L can be reached easily. The optimal sample digestion and the efficient Auto-Protection system, including a high-capacity dryer preventing condensation loss, enable excellent reproducibility.

For lower throughput demands, the compEAct S can be alternatively equipped with LS 1 liquids autosampler or the semi-automatic injection aid AI-SC.



Figure 8: compEAct S with LS2 autosampler

Recommended device configuration

Table 5: Overview of devices and accessories

Article	Article number	Description
compEAct S	450-300.001	Analyzer for the determination of sulfur in liquids and gases
LS 2	450-900.451	Autosampler for liquids
Evolution software	450-011.300	Control and data evaluation software

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 1.0 · Author: AnGr
en · 11/2023

© Analytik Jena | Pictures ©: AdobeStock/scharfsinn86