



Challenge

Easy, automated analysis of sulfur traces in light volatile ultra-pure alcohols, repeatable analysis results at minimum operation and maintenance effort

Solution

Fully automated sample supply, automatic adaptation of combustion process to the specific needs of samples ensuring soot-free combustion

Intended audience

Industrial quality control labs, biofuel production, production of ethanol and methanol

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

Introduction

The term „bioethanol“ refers to ethanol that is used as a fuel or an additive in fuel. It is mainly derived from sugar, starch, or ligno-celluloses by biochemical processes. Sugar can be fermented directly while starch and celluloses require additional process steps to break them down into smaller sugar molecules. Starch and celluloses are so called oligo or polysaccharides. To disaggregate them to monosaccharides enzymatic hydrolysis is used.

Originally, only sugars and starch from food crops, sugar beet, and sugar cane have been used as feedstocks. However, there have been growing concerns that the use of these crops for fuel production will lead to serious competition for these feedstocks, resulting in rising food prices and regional shortages. To prevent this, new feedstock materials and processes for fuel production have been developed. They are based on non-food feedstocks, such as

biomass residue from agriculture, paper, or timber industry (e.g., straw, sugar beet, sawdust, bark, paper waste). This is a better way, but there is still a competing use of agricultural land.

Third-generation biofuels help to overcome this conflict. They are based on non-food materials that are cultivated where agriculture is not possible (e.g., algae in microalgae reactors). Today, algae are used commercially for production of bioethanol. They are especially engineered to ensure maximum yield of starch to make ethanol production profitable. This next generation of sustainable green fuels, helps to further reduce CO₂ emissions.

In the past 10 years, production of ethanol has more than doubled due to increasing demand from the transportation sector, since the quickest way to induce CO₂ footprint reduction is adding sustainable fuels to fossil fuels.

The U.S. Department of Energy cites an analysis conducted by Argonne National Laboratory, which “found that, when entire life cycles are considered, corn and ethanol have reduced greenhouse gas emissions by an average of 34% over traditional fuels. Depending on the feedstock, emission reductions of cellulosic ethanol compared to conventional gasoline, range from 51% to 88% when land-use change emissions are considered.”^[1]

For this purpose different ratios of bioethanol are added. Typical fuel blends are E5, E10, E15, and E85. The number indicates the ratio of the added alcohol in Vol-%. Common cars are able to use these blends up to E10 without adaptations to the engine or fuel system, any other blend requires so called flexible fuel vehicles (FFV). Bioethanol can also be used pure, as E100, but only by special engines. Sulfur is a natural component of biobased feedstocks for production of ethanol unless it is removed during the production process. This is especially important when it is used as a fuel blend component (oxygenate) or pure, as included sulfur compounds contribute to air pollution by SO₂. Like classic fuels they are subject to strict control of their sulfur content and must adhere to the same permissible limits, e.g., 10 ppm in the European Union. Analysis standards and product specifications (ASTM D4806, D5798, DIN EN 15376, 15293) help with this.

Bioethanol in general is a high purity additive. Expected sulfur impurities are nearly 1 ppm S or less. This and the

high oxygen ratio require a very sensitive analysis principle able to detect sulfur amounts in the sub-ng level, unaffected by matrix effects caused by the high oxygen of the sample. Among all sulfur analysis techniques, the combustion elemental analysis with UV-fluorescence detection is best suited for this analytical challenge. The most often applied analysis norms are ASTM D5453, DIN EN ISO 20846, or DIN EN 15486.

Besides fuel production, ethanol can be used in many other ways: directly, like in food production, as beverage, flavor enhancer, or as ingredient in pharmaceuticals and disinfection agents for health protection. In cosmetics it is used as carrier and solvent for creams, cleansers, and perfumes. It is also used in domestic products like detergents, antifreeze and cleaning products, as well as in paints and resin production. Or it is used as a feedstock for 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).

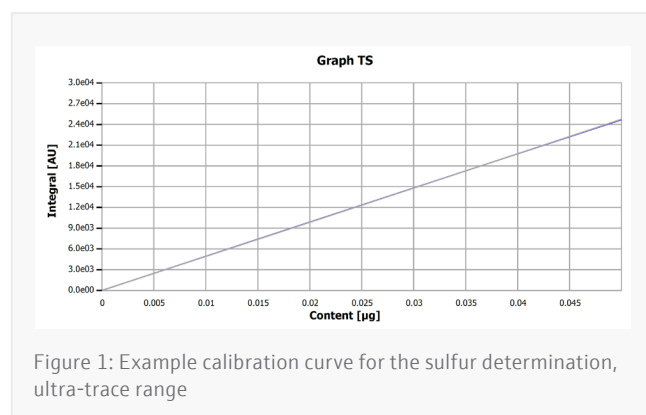
Materials and Methods

Samples and reagents

- Four alcohol samples of different grades, two for ethanol and two for methanol
- Kit calibration solutions 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 pre-treatment.



Calibration

Prior to the measurements the multi EA 5100 was calibrated for sulfur determination. Therefore liquid standards based on dibenzothiophene (S) in isooctane in the concentration range 0.1 to 10 mg/L S were used, a blank correction was applied. The gained calibration was also verified with certified materials. Injection volumes of 40 µL have been applied for the calibration and verification measurements. In figure 1 the calibration curve for ultra-trace range and its performance data is depicted exemplarily.

Table 1: Performance data of sulfur calibration

Parameter	Value
Injection volume	40 µL
Range	0 - 0.05 µg S absolute
Detection limit	3.56 µg/L S
Linearity	linear
Correlation coefficient	0.99999

Instrumentation

A multi EA 5100 analyzer with HiPerSens UVFD for the determination of sulfur was used in vertical operation mode. A multi matrix autosampler type MMS in the liquids mode to enable fully automated injection of the liquid samples by aid of a syringe was applied. For both, samples and standards, a volume of 40 µL was injected. If required, the MMS can be cooled to prevent too early evaporation that could result in sample loss or vigorous combustion. The sample digestion was carried out by efficient catalyst-free high-temperature combustion in a quartz glass tube. Thanks to the quartz pyrolyzer as well as the fully automatic monitoring and adaptation of process parameters, samples are combusted quantitatively.

The process is split into two phases. In the first phase, volatile sample components are evaporized in an inert gas stream. In the second step, the combustion of the formed gaseous products in an oxygen rich atmosphere, takes place. In the second phase the heavier, non-volatile sample components and formed pyrolysis products are quantitatively oxidized in pure oxygen. The implemented auto protection system and the high-performance dryer guarantee the highest operational safety (particle and aerosol trap), as well as a quick and complete transfer of the formed SO₂ to the UV-fluorescence detector without condensation loss. The multi EA 5100 enables a detection limit as low as 5 µg/L S.

Method parameters

For the analysis of standards and samples a method of the standard library was used. The process parameters are summarized in Table 2. The injection volume for the TS determination was set to 40 µL with the help of MMS autosampler.

Evaluation parameters

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

Table 2: Process parameters multi EA 5100 – vertical operation

Parameter	Setting
Furnace temperature	1050 °C
Furnace mode	vertical
2nd combustion	60 s
Ar flow (1st phase)	150 mL/min
O ₂ main flow	200 mL/min
O ₂ flow (2nd combustion)	150 mL/min
Draw up speed	2.0 µL/s
Injection speed	0.5 µL/s

Table 3: Detection parameters for sulfur determination (UVFD)

Parameter	Setting
Max. integration time	360 s
Start	0.2 ppb
Stop	0.5 ppb
Block	7

Results and Discussion

The results obtained for samples and standard solutions are summarized in Table 4. They are average values of three replicate measurements. The methanol and ethanol samples were analyzed easily without any problem. The high repeatability is confirmed by the low RSD values. This is comparable to the quality of analysis of the standard solutions. Their results match the specified concentrations, standard deviations are convincingly low.

A clear finding of the experiments is the fact that depending on the production approach also the content of sulfur containing compounds is affected. A good example for this are the two different ethanol samples.

Table 4: Results of sulfur determination of the given alcohol and standard samples

Sample	$c_s \pm SD$ [mg/L]	RSD [%]
Ethanol 1	2.61 ± 0.01	0.26
Ethanol 2	5.49 ± 0.16	2.01
Methanol 1	0.90 ± 0.02	1.86
Methanol 2	0.85 ± 0.01	1.74
Standard 1.10 mg/L S	1.15 ± 0.01	1.05
Standard 5.00 mg/L S	5.06 ± 0.02	0.45

In the following, typical measurement curves for the sulfur determination of samples and standard solutions are shown.

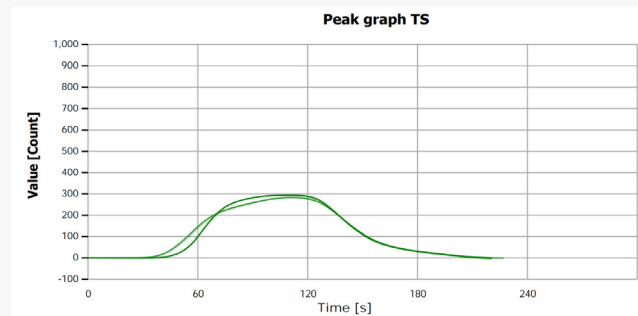


Figure 2: TS measurement curve for sample "Ethanol 1"

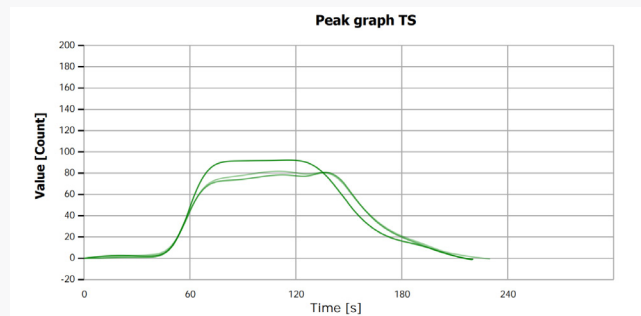


Figure 3: TS measurement curve for sample "Methanol 2"

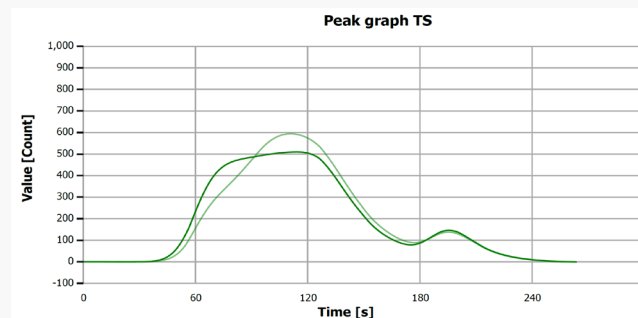


Figure 4: TS measurement curve for "Standard 5.00 mg/L S"

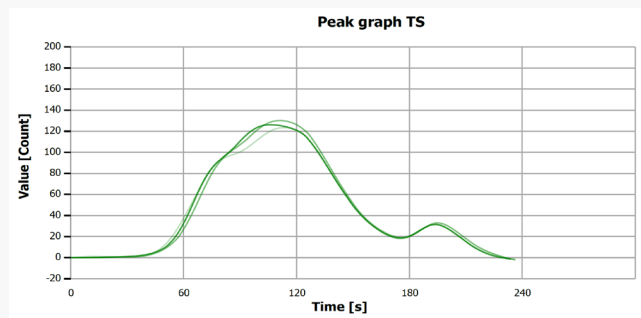


Figure 5: TS measurement curve for "Standard 1.10 mg/L S"

Summary

Using the multi EA 5100 with the MMS autosampler in vertical mode allows for a direct, quick analysis of sulfur traces in light volatile ultra-pure alcohol. Especially for determination element contents close to the detection limit in very volatile hydrocarbons like methanol, the cooling option for sample introduction is an essential advantage to ensure reliable results independent of matrix volatility. Automatic optimization of the combustion process creates ideal digestion conditions for any organic matrix, keeping incomplete combustion and system contamination away. No manual adaptation is required thanks to the ready-to-use standard compliant analysis methods of the analyzer's method library. Just one single method is enough to analyze the full spectrum of the given samples, independent of their concentration. This way, a matrix-specific method development is no longer necessary and best comparability of results is ensured.

If required, the application range of the analysis system can easily be extended by supplementary modules for the determination of nitrogen, chlorine, and/or carbon contents. If only sulfur is in the focus, the compEAct S elemental analyzer is a well-suited alternative, additionally enabling remote operation of the analyzer.



Figure 6: multi EA 5100 with MMS autosampler

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
multi EA 5100	450-300.011	multi EA 5100 – combustion elemental analyzer
C/N/S high performance drier kit	450-300.012	High performance reaction gas drier
S module basic	450-300.021	Extension of multi EA 5100 for sulfur determination with UV-fluorescence
Multi Matrix Sampler	450-300.030	For automatic sample supply
Liquids kit for MMS	450-300.033	Extension of the MMS for automated dosing of liquids
multiWin software	450-011.803	Operation and data evaluation software for multi EA 5100 inclusive method library

References

[1] Ethanol Basics Fact Sheet - U.S. Department of Energy, p. 3

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Version 1.0 · Author: AnGr
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