



Challenge

Quick, concentration-independent sulfur determination in viscous edible oil samples in a vertically arranged analyzer

Solution

The compEAct S offers optimized vertical combustion and efficient gas purification combined with HiPerSens UV-fluorescence detection (UVFD)

Intended audience

Industrial quality control labs in edible oil production, biofuel production, and independent oil control labs and authorities

Determination of Sulfur in Mustard Oil and other Glucosinolate-rich Edible Oils by Combustion Elemental Analysis with UV- fluorescence Detection

Introduction

Sulfur in edible oils is considered an undesirable pollutant that is negatively impacting quality and taste, leading to corrosion of processing equipment and acting as a catalyst poison. In specialty oils however, the sulfur appears naturally and is highly welcome. One of these is mustard oil. It has a long tradition mainly in Asian countries, whether as a cooking or seasoning oil or as an ingredient in medicines and health products. Due to its distinctive taste and its manifold positive health effects, it is very popular. The secret of its effects lies in the remarkably high content of sulfur in the mustard oil, bound in glucosinolates. As the sulfur content and the benefits of the oil correlate, the sulfur content can be used for a quick assessment of the quality and processing of the oil.

Generally, sulfur compounds are determined by special chromatography techniques. This, however, requires

knowledge of each individual compound contained in the oil and an appropriate calibration, which often is very time-consuming. The total sulfur (TS) content of the oil can be determined much faster, i.e. all sulfur compounds are determined together as a sum parameter, without specifying the compounds. Combustion elemental analysis coupled with UV-fluorescence detection is a suitable technique for this, and requires only a single, non-matrix-specific calibration for sulfur quantification.

Combustion elemental analysis is used in many application fields, but the undisputed number one is the petrochemical industry. In this field, a wide range of matrices with different viscosities and sulfur concentrations - from high sulfur crude oils to high purity hydrocarbon products - must be monitored. Well-established analytical standards such as ASTM D5453 or D7183 are therefore used. As matrix

properties and concentrations are nearly equivalent, these standards can also be applied to non-fossil oil matrices. The analytical strategy described below is well suited for rapid quality control in mustard oil production, refining, and downstream processing. Where time is money, a technique which ensures fast and reliable analyses independent of matrix effects is always welcome. In combustion elemental analysis especially the vertical approach enables high throughput, short analysis times, and easy operation.

However, it is not suitable for any matrix. For higher viscosity samples (> 10 cSt), the horizontal approach with boat inlet system has become the standard for combustion elemental analysis. In the experiments described herein, sample dosing and combustion process of a vertical analyzer was adapted to enable reliable results for viscous edible oils in this operation mode.

Materials and Methods

Samples and Reagents

- Samples: different mustard seed oils and rapeseed oil
- Test and control standard: dibenzothiophene in isooctane, c: 10.1 mg/L S, part of the standard kit for calibration and test of compEAct S (Analytik Jena, Art.-No.: 402-889.309)
- Diluent: toluene, SupraSolv® for GC-ECD/FID, Supelco®, (Merck, Art.-No.: 1.08389.1000)

Sample Preparation

The analyzed oil samples are characterized by a higher viscosity (up to $74 \text{ mm}^2/\text{s}$ at 20°C) than classic aliphatic hydrocarbons. When being analyzed with direct sample introduction via syringe, either a dilution with a suited solvent (e.g., toluene), or the utilization of a suited hardware strategy (e.g., special wide bore needle, temperature-controlled injection aid or autosampler) is a must. For the following analysis, both, the dilution strategy, and the usage of a wide-bore needle was chosen.

This allows to compare the results to depict suitability of both strategies for the analyzed matrices. The dilutions have been prepared with toluene as diluent on basis weight/weight, dilution ratio 1:2. To avoid a preceding sample dilution, a third option is possible, even though not applied in these experiments. A heated sample supply system, e.g., autosampler with both, heated syringe and sample tray, could be applied to enable direct injection of samples which are homogeneous, but have an increased viscosity.

Calibration

Liquid calibration standards based on dibenzothiophene in isooctane were used to calibrate the analysis system. For analysis in the ultra-trace level, the calibration range 1 was used, the range 2 was used for trace to middle contents. Figure 2 shows the calibration curve. The correctness of calibration was checked with different standard solutions of known concentration.

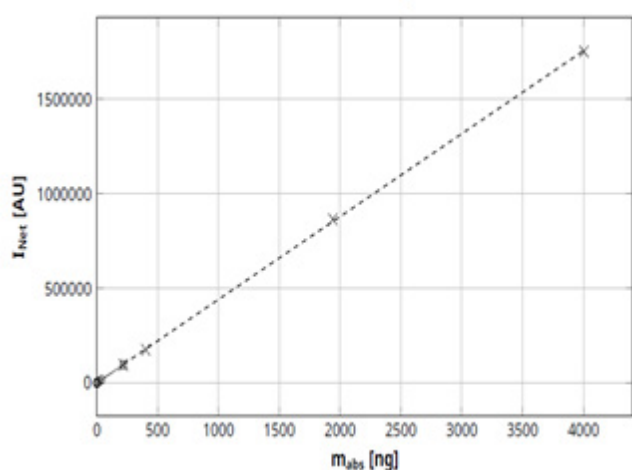


Fig. 1: Calibration curve of used calibration ranges

Table 1: Statistical data of used calibration ranges

Parameter	1	2
Measurement range (μg)	0.0002-0.2188	0.2188-4.0052
Measurement range (AU)	113-95,779	95,779-1,751,203
k_0	36.29	2,881.8
k_1	437,490.5	437,888.1
Coefficient of determination, R^2	1.00000	0.99988
Calculation volume, V_{cal} (μL)	40	40
Detection limit ($\mu\text{g/L}$)	2.59	1,380
Quantification limit ($\mu\text{g/L}$)	9.57	5,828.6
Method standard deviation ($\mu\text{g/L}$)	3.09	589.85
Method coefficient of variation (%)	0.46	1.44
Linearity	linear	linear
Daily factor	1	1

Instrumentation

A combustion elemental analyzer of the type compEAct S in vertical operation mode was used for the analysis. Sample introduction was carried out by an LS 2 liquids autosampler to increase the sample throughput. 40 μL of the diluted as well as pure 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. This tube is equipped with a quartz pyrolyzer, ensuring sharp peak modulation, and thereby maximum sensitivity. Especially for samples with increased viscosity, independent if dosed directly or in dilution, this component is crucial to ensure a controlled, optimum combustion of all sample components without system contamination. The digestion process is bi-phasic. In the first process phase evaporation of light components and pyrolysis of the heavier ones takes place within an inert argon atmosphere.

Method Parameters

For analysis of the liquid standards and samples (diluted and pure) 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 . For direct injection of the pure samples a syringe with wide-bore needle was used, the injection of standard and diluted samples was done by means of the standard μL -syringe. For both the same introduction parameters have been used, no method adaptation was necessary.

Evaluation Parameters

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

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. In this way, concentration specific adaptation of the system or detector is not necessary, saving valuable operation time and material.

Table 2: Process parameters compEAct S

Parameter	Setting
Furnace temperature	1,050 °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	1.0 $\mu\text{L/s}$
Injection speed	0.2 $\mu\text{L/s}$

Table 3: Evaluation parameters compEAct S

Parameter	Setting
Max. integration time	300 s
Start	1 cts
Stop	1 cts

Results and Discussion

The results obtained, are summarized in Table 4. These are average values of tenfold replicate analyses. The diluted samples were analyzed without problems. The higher viscosity of the original matrix did not result in any memory effect, which is confirmed by the low RSD values of only just above 1. This is comparable to the quality of the analysis of the standard material. For direct analysis, RSD values are in the same range, but slightly lower.

The tenfold analysis without outlier selection was performed to check the repeatability of injection and digestion, as such viscous materials are not the simplest sample types for vertical analysis approaches. However, despite all doubts, the results obtained are quite promising for the adaptation of methodology to other homogeneous oil matrices.

Table 4: Results of the TS determination in mustard and rapeseed oil

Sample ID	Dilution		Direct*		Delta (%)
	c_s (mg/L)	SD (mg/L)	c_s (mg/L)	SD (mg/L)	
Mustard oil "Altenburg"	11.0	± 0.16	11.3	± 0.22	2.73
Mustard oil "Solling"	200	± 2.75	188	± 1.52	6.00
Rapeseed oil **	4.51	± 0.07	4.70	± 0.03	4.21
Standard 10.1 mg/L S			10.0	± 0.09	

* syringe with wide-bore needle

** contains also glucosinolates naturally

The differences of diluted and undiluted samples are low and acceptable for such matrix type. Most probably, they are caused by two factors: the dilution process itself (precision of the balance etc.) and different dosing syringes used (dead volume cannula) rather than by the digestion process.

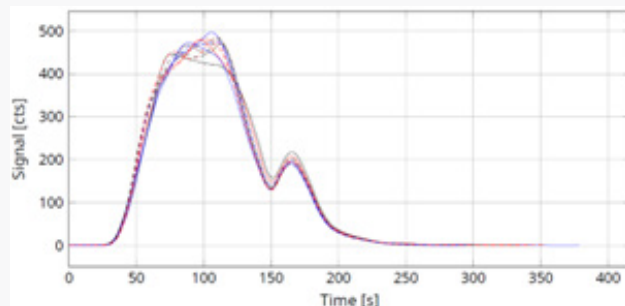


Fig. 2: TS curve, mustard seed oil "Altenburg"

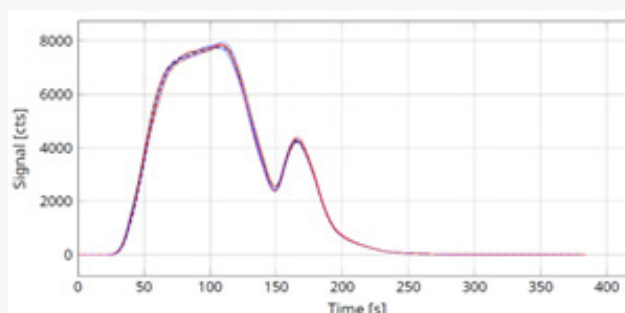


Fig. 3: TS curve, mustard seed oil "Solling"

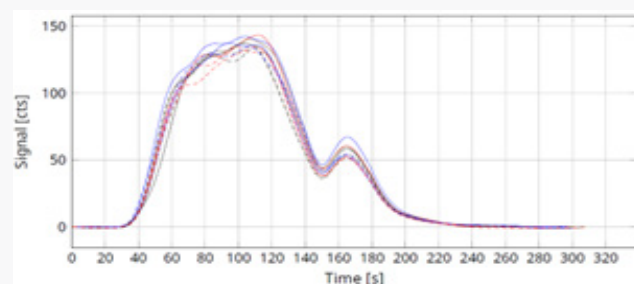


Fig. 4: TS curve, rapeseed oil

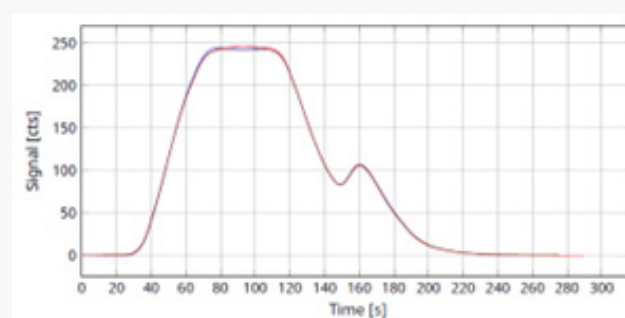


Fig. 5: TS curve, standard, 10.1 mg/L S

Summary

The compEAct S has proven to be well suited for the quick determination of sulfur in viscous edible oil samples. As a vertical system, it is a fast and reliable solution for the precise determination of highly variable sulfur contents even with challenging sample matrices. Thanks to the HiPerSens technology, a measurement range of up to 10,000 mg/L can be easily achieved from a detection limit of only 5 µg/L sulfur. Optimum sample digestion and the efficient auto-protection system, including a high-performance dryer, enable excellent reproducibility, as shown by the low deviations in tenfold repeat analyses. The ability to use different sample introduction strategies (dilution, heated dosing system, etc.) allows the adaptation of the analysis process to the specific requirements of the sample matrix and the preferences of the user. High sample throughput is easily achieved by using the LS 2 or the temperature-controllable LS-T autosampler. For lower throughput requirements, the LS 1 liquid autosampler or the AI-SC autoinjector can be used.



Fig. 6: Analytik Jena compEAct S with LS 2 autosampler

Recommended device configuration

Table 5: Recommended device configuration

Article	Article number	Description
compEAct S	450-300.001	Elemental analyzer for the determination of total sulfur by means of UV-fluorescence detection.
LS 2	450-900.451	Autosampler for compEAct series -for automatic introduction of liquid samples up to 100 µl volume
EAcvolution	450-011.300	Operation and data evaluation software for comEAct series
Standard kit for calibration and test of compEAct S	450-889.309	Calibration solutions sulfur, based on dibenzothiophene in iso octane, from 0.1 – 500 mg/LS

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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

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