Challenge

Automated TS determination in highly viscous oil samples without sample preparation or dilution, reliable analytical results, easy operation and low maintenance

Solution

Elemental analyzer with temperature controlled sample supply, and adaptation of combustion process by intelligent sensor technology

Intended audience

Quality control labs in the edible oils, biofuel and oleochemical industry, as well as independent oil control laboratories and authorities

Fully Automated Determination of Total Sulfur in Different Edible Oils by means of Combustion Elemental Analysis and UV-Fluorescence Detection

Introduction

Edible oils are staple foods and irreplaceable raw materials for many industries. Besides food preparation and the production of processed foods, they are used for cosmetics, biofuels, oleochemicals and pharmaceuticals. To protect consumers and the environment, standards and guidelines ensure the continuous monitoring of their quality and safety parameters along the value chain. Given the sheer volume of edible oil to be analyzed and the complexity of production, industrial laboratories of food and drug manufacturers as well as laboratories of government agencies face the challenge of obtaining reliable analytical data for high sample quantities in the shortest possible time. In addition to metal and heavy metal traces, sulfur, nitrogen and chlorine often need to be determined. These elements are usually not natural components of edible oils but enter as impurities. They can affect the production process, quality,

and properties of the final product by affecting odor, color, taste and shelf life. Some even contribute to the formation of toxic compounds. Testing of these parameters is necessary not only for quality but also for safety reasons. Often their concentration range is in the ppb or low ppm range. Sulfur occupies a special position. Undesirable as an impurity in many oils, it may be a quality indicator in others. Such oils are often obtained from the seeds of cruciferous plants (brassiceae). They naturally contain organically bound sulfur in the form of glucosinolates which form allyl thiocyanates during their enzymatic degradation process. These compounds not only give the oil an interesting flavor, but are also popular for their aseptic, disease-preventive and other health effects. Well-known representatives are mustard seeds, cabbage, radish, cress or capers, whose oils are used in natural medicine and food supplements.

analytikjena

An Endress+Hauser Company

Determination of total sulfur as a sum parameter (TS) has proven useful in both tasks when rapid control of sulfur content is required. Elemental analysis coupled with UV-fluorescence detection is a suitable technique for this purpose and requires only a single, non-matrix specific calibration for the quantification of sulfur. The technique provides a wide measurement range on matrices of varying viscosity. It has long been used successfully in the chemical and petrochemical industries and is described in detail in local and global standards, including ASTM D5453 for challenging matrices such as mineral oil. Edible oils share many common features with mineral oil and related samples such as high viscosity, high boiling points and very long-chain or saturated hydrocarbons. Therefore, this ASTM standard can easily be adapted for the analysis of edible oils. If more precise information on the nature of the sulfur compound is required, chromatographic methods are recommended. Here, a particular compound can be accurately quantified in the presence of all other sulfur-containing substances. The following analysis of a representative spectrum of various vegetable oils shows how easily combustion elemental analysis can be adapted for the pretreatment-free, sensitive and precise determination of sulfur over the entire concentration range.

Materials and Methods

Samples and reagents

- 14 edible oil samples from different processing stages (starting materials, intermediates, end products) and different production processes (cold pressed, solvent extracted, refined, hydrogenated) as well as a high purity reference oil (paraffine oil)
- Kit calibration solutions, c: 0.1 – 10 mg/L S, Analytik Jena GmbH+Co. KG, 402-889.070
- Kit calibration solutions, c: 10 – 100 mg/L S, Analytik Jena GmbH+Co. KG, 402-889.167
- Kit calibration solutions, c: 100 – 500 mg/L S, Analytik Jena GmbH+Co. KG, 402-889.164

Sample preparation

The samples and standards were analyzed directly without sample pretreatment. The use of a heated supply system, e.g., a temperature-controlled liquid sampler, allowed for direct injection with a syringe. Heating to 75 °C significantly reduced the viscosity of the sample. This is possible when dealing with homogeneous liquids with increased viscosity.
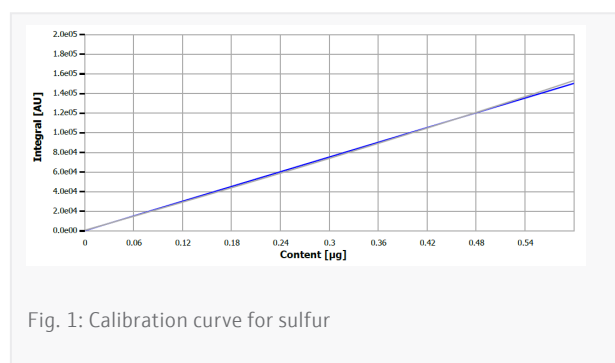
Another approach is to dilute the samples with a suitable solvent to reduce viscosity and allow automatic sample supply without a special sampler. This strategy is not part of the experiments described here.

Calibration

Prior to the measurements the multi EA 5100 was calibrated for sulfur determination. For this purpose, liquid standards based on dibenzothiophene (S) in isooctane in the concentration range 0.1 to 500 mg/L S were used and a blank correction was performed. The obtained calibration data were verified with certified reference standards. 40 µL injection volume were used for the calibration and verification measurements. Figure 1 shows the calibration curve for the ultratrace range, its performance data are summarized in Table 1.

Fig. 1: Calibration curve for sulfur

Table 1: Calibration performance parameters

Parameter	Value
Injection volume	40 µL
Concentration range	0-0.4 µg S abs.
Detection limit	5.99 µg/L
Linearity	linear
Correlation coefficient	0.9996

Instrumentation

A multi EA 5100 analyzer equipped with a HiPerSens sulfur detector was used in horizontal operation mode. For automated sample introduction and transfer into the analyzer, the system was equipped with an automatic boat drive with flame sensor technology and with the temperature-controlled multi matrix sampler MMS-T. The MMS-T enables cooling for automated dosing of extremely light volatile liquids, or heating for direct dosing of viscous homogeneous liquids without prior dilution. The flame sensor ensures trouble-free and matrix-optimized transfer and combustion of the different materials. For sulfur determination, a volume of 40 µL of the sample or standard was used. Sample digestion was carried out by efficient catalyst-free high-temperature combustion in a quartz tube.

Method parameters

For the analysis of liquid standards and oil samples, a method from the method library was used. The method parameters are summarized in Table 2. The injection volume for the TS determination was set to 40 µL. For the direct injection of the pure samples, a temperature-controlled syringe was used. During the entire analysis time, both the syringe and the sample (sample tray) were kept at a constant temperature of 75 °C. This allows direct injection that is independent of the original sample viscosity, thus avoiding time-consuming and error-prone dilution steps.

The measurement process is controlled and fully automatically adapted to the needs of every matrix component by the flame sensor technology. This ensures matrix-independent, optimal results in the shortest possible time. The process is split into two phases. In the first phase, the volatile sample components are evaporated in an inert gas stream, followed by the combustion of the formed gaseous products in an oxygen-rich atmosphere. In the second phase, the heavier, nonvolatile sample components and formed pyrolysis products are quantitatively oxidized in pure oxygen. An implemented auto protection system guarantees highest operational safety (particle and aerosol trap). A detection limit of 5 µg/L can be reached easily.

Table 2: Process parameters multi EA 5100 – horizontal operation

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 phase)	200 mL/min
Draw up speed	2.0 µL/s
Injection speed	2.0 µL/s
ABD mode	automatic*

* flame sensor controlled automatically optimized combustion

Evaluation parameters

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

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

Parameter	Setting
Max. integration time	720 s
Start	0.1 ppb
Stop	0.1 ppb
Block	7

Results and Discussion

The results obtained for samples and standard solutions are summarized in Table 4. They are the average values of three replicates. No problem occurred while analyzing the edible oil samples, and no memory effect was detected, which could have been caused by the higher viscosity of the samples. The low RSD values of the sample measurement were comparable to the measured values of the standard solutions and confirm the high reproducibility of the results. Even for samples like almond oil, in which sulfur impurities occur only in the ultratrace range, the quality of the results was convincing. This indirectly confirmed the repeatability of the injection and the optimal digestion process. In addition to the analysis of edible oil, the measurement method could also be used for other homogeneous oils and comparable matrices (such as UCO, tall oil or cod liver oil, glycerol).

Table 4: Results of Total Sulfur determination for the edible oil samples and standards

Sample	c_s [mg/L]	RSD [%]
Mustard oil, native	234	1.60
Linseed oil	40.8	0.50
Mustard oil 2	14.4	0.07
Mustard oil*	3.86	1.95
Rice bran oil	3.67	2.53
Walnut oil	2.88	0.76
Palm oil raw	2.75	0.40
Rapeseed (canola) oil	1.85	1.48
Sesame oil	0.81	0.75
Peanut oil	0.76	0.85
Coconut oil	0.47	3.01
Olive oil	0.38	4.83
Almond oil	0.19	1.32
Paraffin oil SA	1.43	0.44
Standard 0.51 mg/L S	0.51	0.91
Standard 5.00 mg/L S	5.00	2.31

* refined

The experiments clearly showed that the production and processing methods also influence the content of sulfur-containing compounds. This is clearly shown by the three different mustard oil samples: While the native mustard oil produced by cold pressing still contains a high amount of sulfur compounds, the other two mustard oils have significantly lower concentrations. In the sample „mustard oil 2" sulfur content is 16 times lower and in the sample „mustard oil", which is a refined oil, sulfur concentration is even lower, only traces are detected.

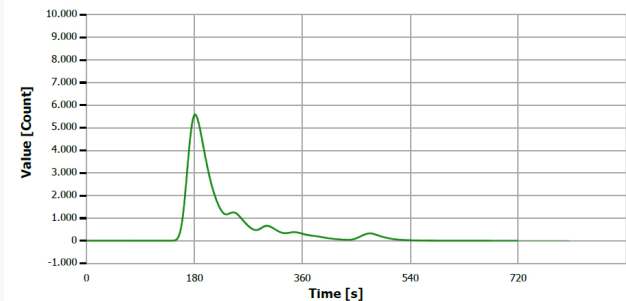In the following typical measurement curves for selected oil samples and standard solutions are shown.

Fig. 2: TS measuring curve for sample "lineseed oil"
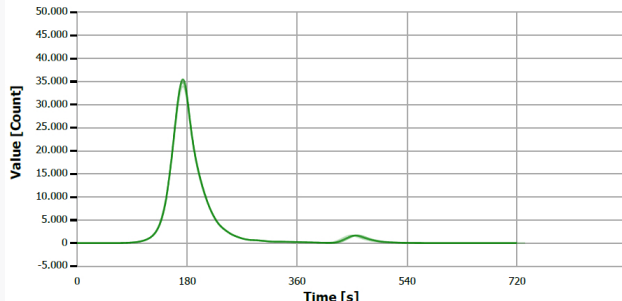

Fig. 3: TS measuring curve for sample "mustard oil, native"
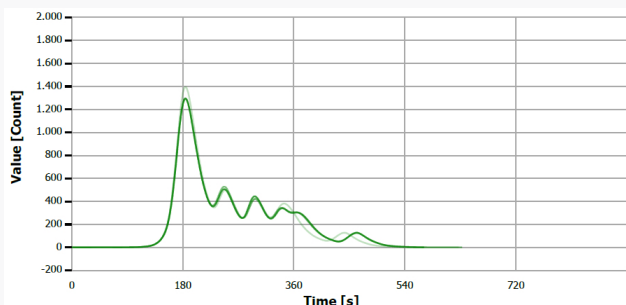

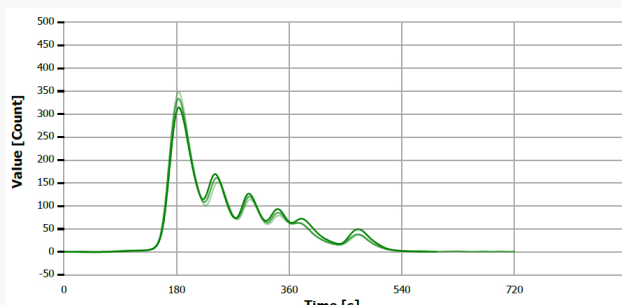Fig. 4: TS measuring curve for sample "mustard oil 2"

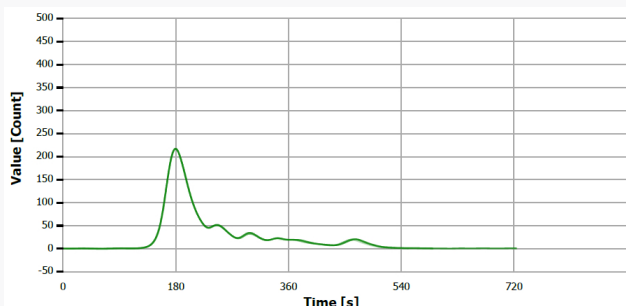Fig. 5: TS measuring curve for sample "mustard oil"

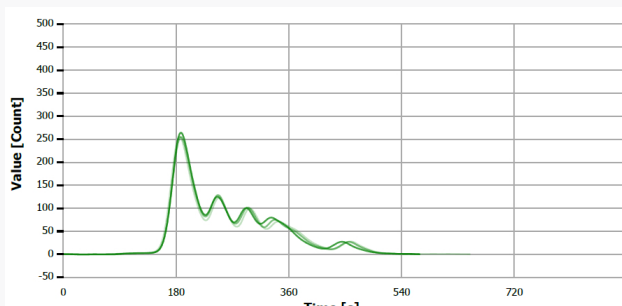Fig. 6: TS measuring curve for sample "rapeseed oil"
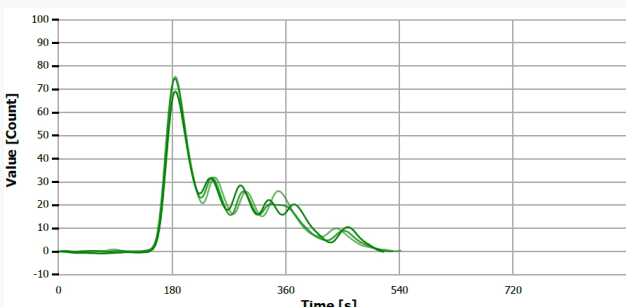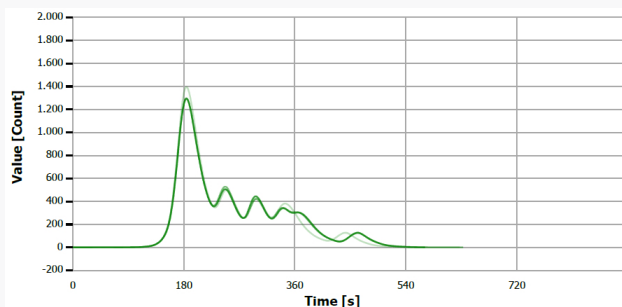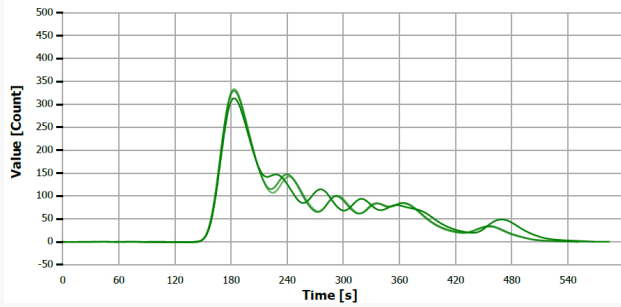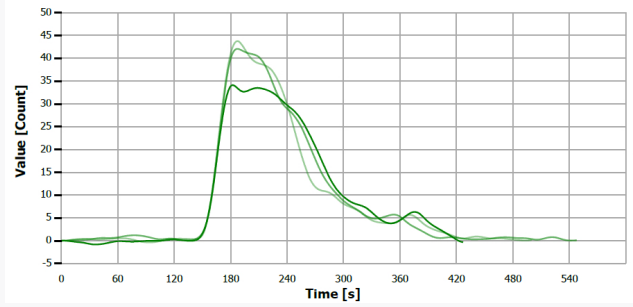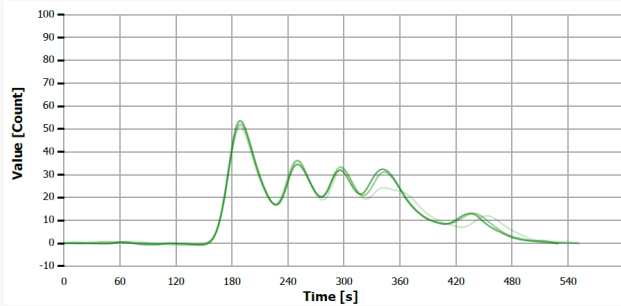

Fig. 7: TS measuring curve for sample "walnut oil"

Fig. 8: TS measuring curve for sample "sesame oil"

Fig. 9: TS measuring curve for sample "palm oil"

Fig. 10: TS measuring curve for sample "rice bran oil"

Fig. 11: TS measuring curve for sample "coconut oil"

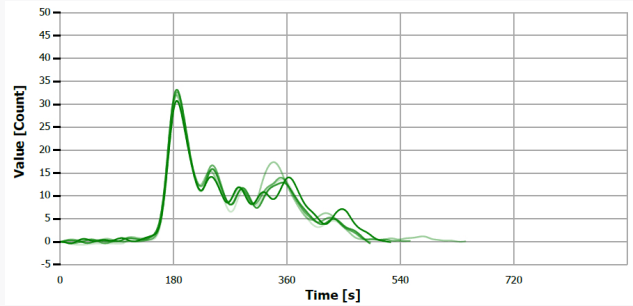Fig. 12: TS measuring curve for sample "peanut oil

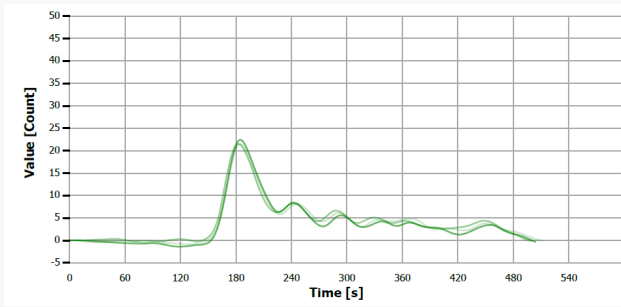Fig. 13: TS measuring curve for sample "olive oil"

Fig. 14: TS measuring curve for sample "almond oil"
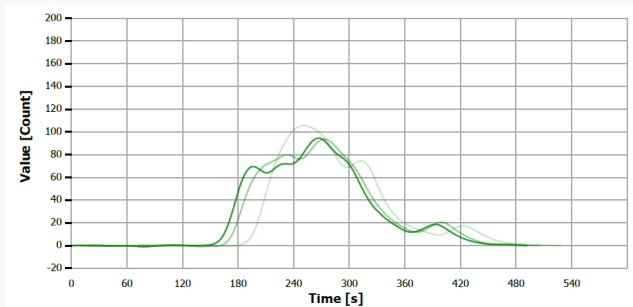

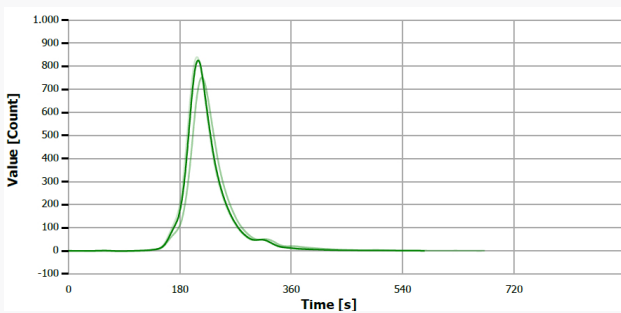Fig. 15: TS measuring curve for sample "paraffine oil"

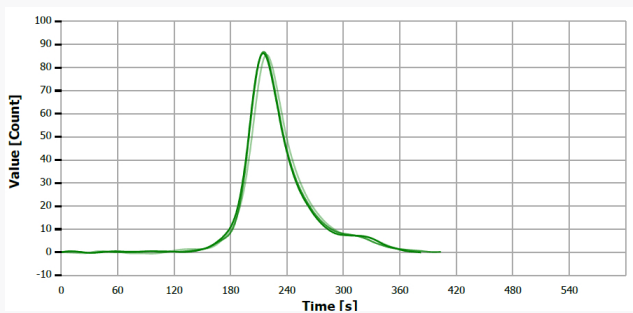Fig. 16: TS measuring curve for standard "5 mg/L S"

Fig. 17: TS measuring curve for standard "0.51 mg/L S"

Summary

Using the multi EA 5100 with MMS-T autosampler in horizontal mode allows for a direct, time-optimized analysis of viscous sample matrices, as is the case with edible oils. Thanks to the efficient heating of sample tray and dosing syringe of this liquids autosampler, viscous matrices can be dosed without a prior dilution step. This saves valuable operation time and money while reducing solvent waste and risk for operator mistakes. Especially for determination of ultra-low element contents close to detection limit, this feature is essential to ensure trustable results. The flame sensor aided, fully automatic optimization of the combustion process creates ideal digestion conditions for any organic matrix. This avoids incomplete combustion and system contamination away, no manual adaptation or specific boat programs are required. Just one single method is enough to analyze the full spectrum of liquid matrices, independent of their viscosity, volatility, combustibility, and concentration. 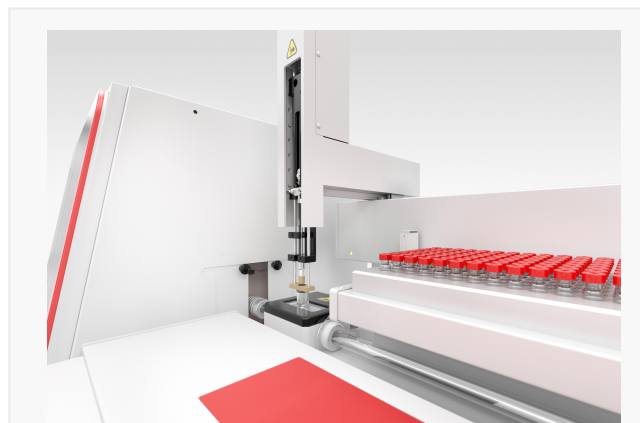This makes matrix-specific method development and calibration redundant, best comparability of results is ensured. If required, the application range of the analysis system can easily be extended by accessory modules for determination of nitrogen, chlorine and/or carbon contents.

Fig. 18: multi EA 5100 with ABD and MMS autosampler

Recommended device configuration

Table 5: Overview of devices and accessories

Article	Article number	Description
multi EA 5100	450-300.011	multi EA 5100 – combustion elemental analyzer for sulfur, nitrogen, chlorine, and carbon analysis in solids, liquids, gases
C/N/S high performance drier kit	450-300.012	High performance reaction gas drier for analysis of carbon, nitrogen and sulfur
S module basic	450-300.021	Extension of multi EA 5100 for sulfur determination with UV-fluorescence
ABD	450-300.013	Automatic boat drive with flame sensor technology – for horizontal operation of multi EA 5100
MMS-T	450-900.453	Temperature-controlled autosampler – heating /cooling option for liquids, extendable for solids analysis
multiWin software	450-011.803	Operation and data evaluation software for multi EA 5100