



### Challenge

Fully automated, fast and accurate determination of nitrogen, sulfur and chlorine trace contents in soy oil

### Solution

Elemental analysis – direct, matrix-optimized combustion coupled with element-selective detection systems

### Intended audience

Quality control labs in soy oil mills and refineries; importers, exporters, and further processors of soy oil; independent oil control labs and authorities

## Extended Quality Check for Soy Oil - Determination of Nonmetal Elements Nitrogen, Sulfur and Chlorine by Combustion Elemental Analysis

### Introduction

Soy oil takes the second place in the global production of vegetable oils, with a projected volume of 60.91 millions of tons in the year 2022/2023 and a share of over 30 %. Its main areas of cultivation are particularly in North and South America, as well as in Asia. Soy oil is used pure for the preparation of cold and hot dishes, as an ingredient in food production, but also in the industrial sector: It is continuously gaining popularity in the energy sector as a feedstock for biofuels (HVO, green diesel, SME), and has long been established in the oleochemical industry in the production of lubricants, adhesives, paints, cosmetics and much more. Soy oil as a food product is subject to strict controls. Quality specifications of the product include physical parameters such as density or viscosity, chemical parameters such as iodine value and acidity, but also trace metal impurities and speciation of compounds. Their presence in the final product is regulated by standards. For their determination,

techniques such as chromatography or spectrometric methods like ICP-OES or AAS are used. In addition to the standardized product quality and safety parameters, parameters that help evaluate the refinery process must be monitored. They are often not standardized, and yet have high informative value about the effectiveness of process steps, possible risks in the formation of unwanted by-products or contamination by auxiliary materials. These process parameters also include the summary content of the nonmetal elements nitrogen (N), sulfur (S) or chlorine (Cl). For example, chlorine in edible oil can contribute to the formation of hazardous 3-MCPD esters when exposed to high temperatures, such as during deodorization. As catalyst poisons, N/S/Cl compounds can, for example, impair the effective hydrogenation of edible oils, shorten the service life of catalysts or cause problems by forming deposits, so-called “fouling” at other points in the process. Therefore, their presence must be monitored at key process steps. When

soy oil is used in fuel production, this applies in particular to sulfur (S), as statutory limits for sulfur emissions must be complied with. For example, 10 ppm S is the limit specified in the EU, which also applies to biodiesel, renewable diesel, HVO and soy methyl ester (SME). For the determination of sulfur, nitrogen and chlorine trace impurities in purely organic matrices, combustion-based elemental analysis is established as the most efficient, fastest, and matrix-independent method. In this method, the three elements are determined after separation of the other matrix components by a catalyst-free high-temperature combustion with selective detection principles, preferably fully automatically.

Sulfur is determined by UV fluorescence, nitrogen by chemiluminescence and chlorine by coulometric titration. A typical representative of such an analyzer is the multi EA 5100. In addition to a high degree of automation and very low detection limits, the system solves two further problems encountered in the combustion of oils. The heated sample feed eliminates the need for the usual but time-consuming and often error-prone dilution prior to analysis, and the flame sensor avoids excessively low, highly fluctuating or incorrect results that can be caused by an incomplete combustion from the outset.

## Materials and Methods

### Samples and reagents

- Three different soy oil samples (food)
- Kit calibration solutions, conc.: 0.1 – 10 mg/L S, Analytik Jena GmbH+Co.KG, 402-889.070
- Kit calibration solutions, conc.: 0.1 – 10 mg/L Cl, Analytik Jena GmbH+Co.KG, 402-889.071
- Kit calibration solutions, conc.: 0.1 – 25 mg/L N, Analytik Jena GmbH+Co.KG, 402-889.075

### Sample preparation

The samples and standards were analyzed directly without sample pretreatment. The use of a temperature-controlled liquid sampler allows direct injection with a syringe. Heating to 80 °C significantly reduces the viscosity of the sample. This is possible when dealing with homogeneous liquids with increased viscosity.

Prior to sample measurement, the multi EA 5100 was calibrated. Liquid standards were used to calibrate the analysis system in the concentration range from 1 to 10 mg/L for each element. For sulfur and nitrogen determination the system was calibrated with dibenzothiophene (S) and pyridine (N) in isooctane as solvent. For the chlorine determination 2,4,6-trichlorophenol (Cl) in isooctane was used. Blank correction was applied to ensure best results for trace analysis. The gained calibrations were verified with certified reference standards. 100 µL (Cl) and 40 µL (N/S) injections have been applied for the calibration and verification measurements. In figure 1 to 3, the calibration curves for ultra-trace range are depicted, table 1 summarizes their performance data.

### Calibration

Table 1: Calibration – Performance parameters

Parameter	Sulfur	Nitrogen	Chlorine
Injection volume	40 µL	40 µL	100 µL
Range	0 – 0.4 µg	0 – 1.0 µg	0 – 1.0 µg
Detection limit	5.99 µg/L	1.98 µg/L	19.94 µg/L
Linearity	linear	linear	linear
Correlation coefficient	0.9996	0.9996	1.0000

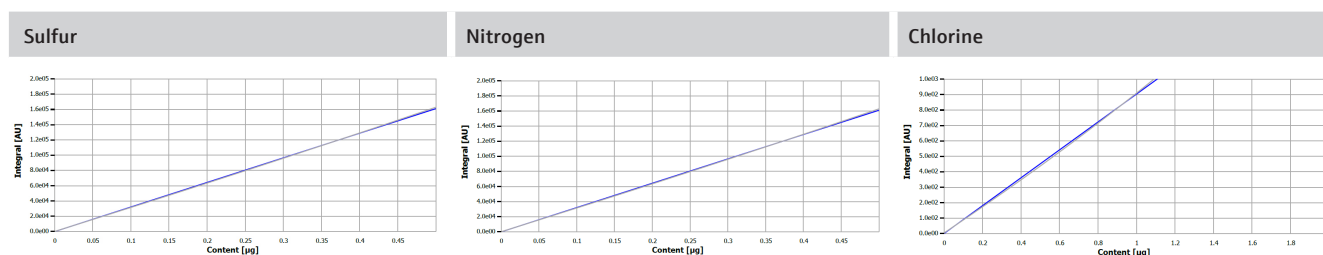


Fig. 1: Calibration curve for sulfur

Fig. 2: Calibration curve for nitrogen

Fig. 3: Calibration curve for chlorine

### Instrumentation

A multi EA 5100 equipped with HiPerSens detection units, UV-fluorescence detector (UVFD) for sulfur, CLD for nitrogen and coulometric titration with “high sensitive” option for chlorine, was used in horizontal operation mode. For the automated sample introduction and transfer into the analyzer the system was equipped with an automatic boat drive with flame sensor technology and the MMS-T, a temperature-controlled multi matrix sampler. The MMS-T can either be cooled to enable automated dosing of extremely light volatile liquids, or – in this case – heated enable direct dosing of highly viscous homogeneous materials without pretreatment by dilution. The liquid samples resp. standards were dosed by the MMS-T into a quartz sample boat, which then was transferred automatically into the combustion furnace. Thereby the flame sensor ensures a trouble-free and matrix-optimized evaporation and combustion of the different materials. Sample digestion was carried out by catalyst-free high-temperature combustion in a quartz tube. This process is controlled and adapted fully automatically to the special requirements of every matrix component by the flame sensor technology. This ensures matrix-independent, optimal results in the shortest possible time. The process has two phases. In the first process phase, 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. The implemented Auto-Protection and drying systems guarantee highest operational safety (particle and aerosol trap) and a complete transfer of the formed SO<sub>2</sub>, NO<sub>x</sub> and HX to the related detection units without condensation loss. The multi EA 5100 enables to determine all three elements in just one analysis cycle, manual system reconfiguration between N/S and Cl analysis is not required. The used multi-element configuration enables detection limits of 5 µg/L S, 10 µg/L N and 50 µg/L Cl.

### Instrument settings

#### Method Parameters

For the analysis of liquid standards and oil samples, a standard method from the method library was used. The method parameters are summarized in Table 2. The injection volume for the S and N determination was set to 40 µL, and for Cl to 100 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 80 °C. This allows direct injection even for samples with high viscosity, thus avoiding time-consuming and error-prone dilution steps.

Table 2: Combustion parameter

Parameter	Specification
Furnace temperature	1050 °C
2 <sup>nd</sup> combustion	60 s
Ar flow (1 <sup>st</sup> phase)	200 mL/min
O <sub>2</sub> main flow	200 mL/min
O <sub>2</sub> flow (2 <sup>nd</sup> combustion)	200 mL/min
Draw-up speed	1 µL/s
Injection speed	2 µL/s
ABD	automatic*

\* flame sensor controlled automatically optimized combustion

## Evaluation Parameters

The evaluation parameters for the detection systems used are summarized in Table 3.

Table 3: Detection parameter

Parameter	Specification		
	Chlorine	Nitrogen	Sulfur
Max. integration time		800 s	800 s
Max. titration time	1200 s		
Start	n.a.*	0.7 cts	0.5 cts
Stop	n.a.*	0.2 cts	0.5 cts
Stability	n.a.*	7	7
Cell cooling	23 °C	n.a.*	n.a.*
Titration delay	1	n.a.*	n.a.*
Threshold	25	n.a.*	n.a.*
Threshold value	300	n.a.*	n.a.*

\* not applicable for this element

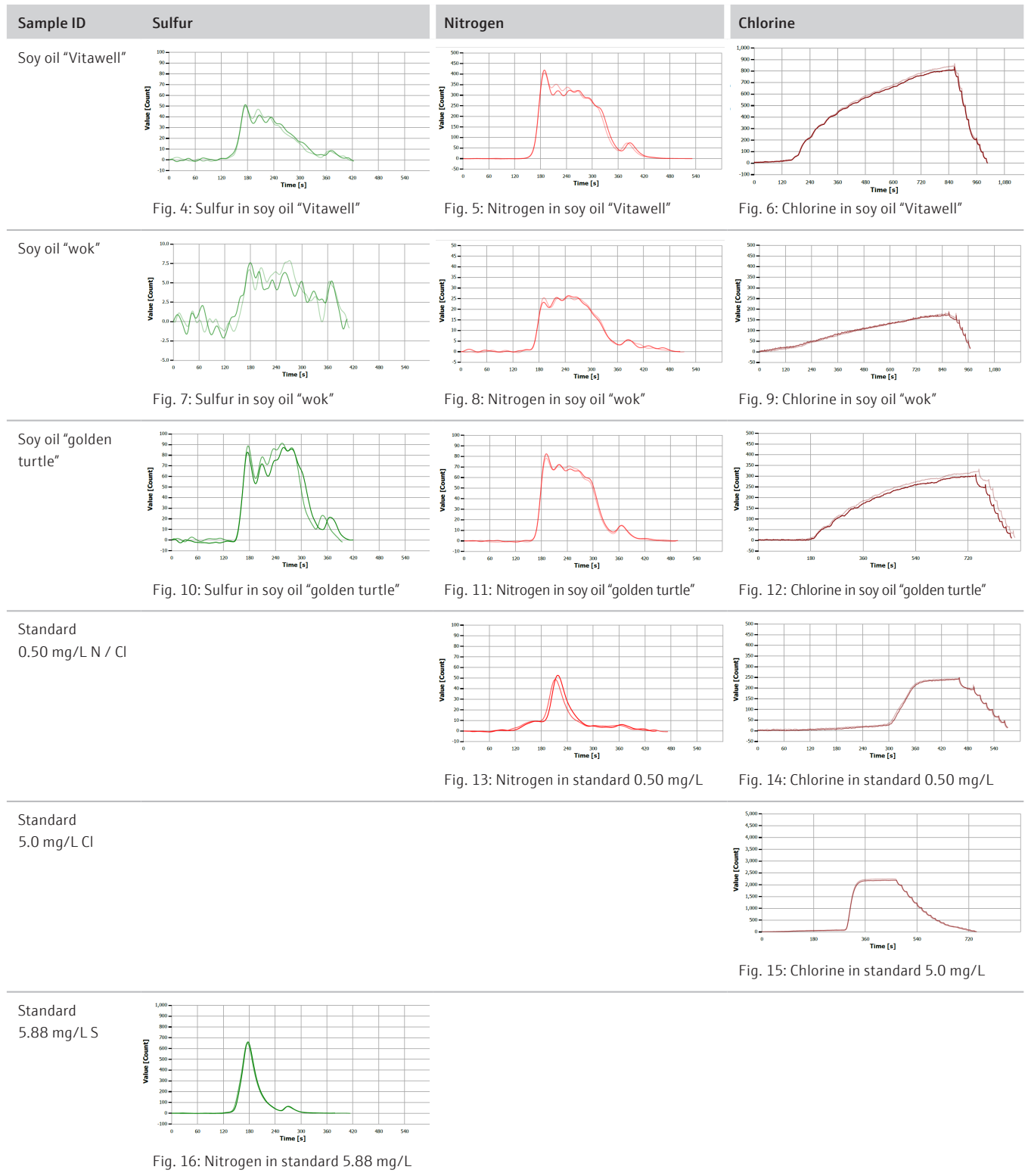
## Results and Discussion

The results obtained for samples and standard solutions are summarized in Table 4. They are average values of three replicate analyses. The soy oil samples could be analyzed easily without any problem. Despite their higher viscosity, there was no memory effect detected. The high repeatability is confirmed by the low SD values. This is comparable to the quality of analysis of the standard solutions. Besides soy oil, this methodology could be adapted for analysing other homogeneous oils and comparable matrices (e.g., palm oil, sunflower oil, UCO (used cooking oil), tall oil, cod liver oil, or glycerol).

Table 4: Results for N/S/Cl analysis of different soy oils and standards

Sample ID	Concentration $\pm$ SD [mg/L]					
	Sulfur		Nitrogen		Chlorine	
Soy oil "Vitawell"	1.12	$\pm$ 0.03	8.61	$\pm$ 0.05	1.36	$\pm$ 0.03
Soy oil "wok"	0.21	$\pm$ 0.01	0.67	$\pm$ 0.00	0.39	$\pm$ 0.02
Soy oil "golden turtle"	2.46	$\pm$ 0.00	1.67	$\pm$ 0.03	0.68	$\pm$ 0.01
Standard 0.50 mg/L N	n.a.	n.a.	0.56	$\pm$ 0.00	n.a.	n.a.
Standard 0.50 mg/L Cl	n.a.	n.a.	n.a.	n.a.	0.51	$\pm$ 0.00
Standard 5.88 mg/L S	5.90	$\pm$ 0.05	n.a.	n.a.	n.a.	n.a.
Standard 5.0 mg/L Cl	n.a.	n.a.	n.a.	n.a.	4.77	$\pm$ 0.00
Isooctane (blank)	0.014	$\pm$ 0.001	n.a.	n.a.	n.a.	n.a.

The "Vitawell" is a cold-pressed oil, thus its content of secondary plant substances is still high. This can be seen from the higher values for non-metal elements contained in these compounds. Especially the N content, which is a component of most B vitamins is high here. Other extraction processes and heavy treatment, such as refining the oil, result in a loss of these compounds, as is the case with the "wok" oil sample. It has the lowest N, S and Cl contents of all the oils examined. The Cl content is low in all samples studied, indicating a low health risk due to the formation of toxic halogen compounds (e.g., 3-MCPD). The corresponding measuring curves for the soy oil samples and standards are shown in the following:





## Summary

Using the multi EA 5100 with MMS-T in horizontal mode allows for a direct, time-optimized analysis of viscous sample matrices, such as soy oil is one. Thanks to the efficient heating of sample tray and dosing syringe of this liquids autosampler, viscous matrices can be dosed without subsequent dilution steps. 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 fully automated optimization of the combustion process, supported by the device's flame sensor, creates ideal digestion conditions for any organic matrix. It also prevents incomplete combustion and system contamination, manual adaptation or specific boat programs are not 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



Figure 17: multi EA 5100 with ABD and MMS autosampler

development and calibration redundant, best comparability of results is ensured. If required, the application range of the analysis system can easily be extended for determination of carbon contents.

### Overview over devices and consumables

Table 5: Used system configuration

Article	Article number	Description
multi EA 5100 BU	450-300.011	Combustion unit
C/N/S High Performance Drier Kit	450-300.012	Reaction gas drying
Cl module 5100	450-300.023	Chlorine detection acc. coulometric titration
Extension kit Cl "high sensitive"	450-300.024	For determination of very low Cl concentrations
S module 5100 basic	450-300.021	Sulfur detection acc. UV-fluorescence
N module 5100	450-300.022	Nitrogen detection acc. chemiluminescence
multiWin Software	450-011.803	Data evaluation and operation software
ABD	450-300.013	Automatic boat drive with flame sensor for soot-free combustion
MMS-T	450-900.453	Temperature controllable autosampler

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