



Challenge

Quick and automated analysis of sulfur, chlorine, and nitrogen traces in highly viscous fatty acid mixes without extensive method development

Solution

Automated sample supply and quantitative, automatically matrix-optimized combustion process

Intended audience

Processors and recyclers of used cooking oils and animal fats, producers of alternative, derived, and biofuels, oleochemicals production, oil regeneration, industrial quality control labs, contract labs

Determination of Total Sulfur, Total Nitrogen, and Total Chlorine Contents in Used Cooking Oil (UCO) and Related Bio-borne Fats by Means of Combustion Elemental Analysis

Introduction

Used cooking oil (UCO) is an umbrella term covering all used vegetable oils, animal fats, and processed oils, which have been used in the food processing industry, hotels, restaurants, home-cooking or frying, and abattoir waste. Regardless of their origin, the major components of all oils are glycerides, esters of the saturated or unsaturated fatty acids and glycerol, accompanied by water, particles, and residues of the processed food. UCO is not classified as dangerous good. However, if it is disposed improperly, e.g., via the sink with the wastewater, the drainage system can be negatively affected by clogging due to solidification of the oil or fat. Even worse can happen if the used oil, together with other „solid waste“, forms huge lumps, so called fatbergs. This often results in a complete blockage of sewage pipes. More than 20% of organic pollution in our waters can be

traced back to improper disposed UCO and related waste materials.^[1]

This is why UCO must be disposed properly. In the best case it is collected, refined, and used in a variety of applications. It can be used for power and heat generation directly, as an additive in animal feed, or for production of biofuels and derived fuels, as well as oleochemicals.

During the last decade, used cooking oil has become more and more attractive for the industry. It underwent a huge transformation – from an undesired environmentally critical waste material to a coveted raw material for more sustainable transportation fuels (e.g., renewable diesel, renewable aviation fuel) and production of organic chemicals and specialties (e.g., paints, solvents, cleansers, lotions, plastics). In 2022, the global market capacity for used cooking oil was valued with roughly 635 million €

with a sustainable growing potential over the next few years. UCO is widely available; the majority is used as a low-carbon feedstock for biofuels. It is ideal for meeting existing biofuel mandates in Europe and the United States, Asian countries have been exporting UCO to these regions increasingly. In the European Union (EU), the Renewable Energy Directive (RED II) incentivizes the use of UCO biofuel to meet renewable energy targets in transport. Proposals to incentivize the use of renewable fuels in the aviation and marine sectors, ReFuelEU Aviation and FuelEU Maritime, are likely to stimulate additional demand for UCO in Europe.^[2] At the same time, the demand for UCO for biofuel within Asia is increasing, as well. The biggest exporters of UCO globally are China, India, Indonesia, Japan, Malaysia, and the Republic of Korea, all located in the Asia Pacific region.

The utilization of UCO as a renewable raw material is advantageous. It reduces dependence on fossil resources, the CO₂ emissions are decreased, which contributes to climate protection. But for this purpose, the UCO must be free of hazardous elements and compounds, which could affect further processing steps, by fouling, corrosion or even worse catalyst poisoning, and generation of undesired by-products. This requires sufficient treatment and cleaning of the feedstocks, for example by filtration, centrifugation, or distillation. Only oils and fats which meet the quality requirements, that means they are free of huge quantities of dangerous impurities like organically bound chlorine, sulfur, or nitrogen compounds, which could have enriched in the oil during usage, can be used for further processing. To ensure this, a robust and highly sensitive matrix-independent analysis technique is needed, able to deliver all relevant results together in the shortest possible time. Fatty acids are not an easy matrix due to their high viscosity, extremely long chains and their partial saturation, their combustion behavior, and the partially inhomogeneous distribution of contaminants inside the used cooking oils.

While other techniques such as X-ray fluorescence analysis (XRF) or combustion ion chromatography (CIC)

already reach their limits in covering the relevant element combination with required sensitivity, combustion based elemental analysis, a versatile applicable technique, which was originally established for determination of non-metal elements in the field of refineries and chemical industry, allows for the determination of the three elements N/S/Cl with a single instrument.

Sample introduction and combustion process must be optimized to ensure correct results. If combustion is not quantitative, soot and other pyrolysis residues are formed inside the analyzer. The transfer of the formed reaction gas is affected, resulting in too low, arbitrary scattering, false results, and a remarkably increased maintenance effort. This is especially important for chlorine analysis.

For such a challenging analysis task, the multi-element analyzer multi EA 5100 is perfectly suited. Due to intelligent valve technique and the modular design all relevant parameters can be measured in one analysis cycle. Nitrogen and sulfur are determined simultaneously. The chlorine content is measured sequentially, fully automatically, without manual system reconfiguration. Thanks to its wide linear measuring range and low detection limits, the multi EA 5100 can be used not only for control of the UCO as feedstock, but also for the purified oils or even the ultra-pure biofuels and chemicals which could be produced based on then UCO. Analysis methods often used therefore are ASTM D5762, ASTM D5453, UOP 779, just to name few.

Due to the great demand, fraud can happen as well. That means that virgin vegetable oils are sold off as UCO. Continuous analysis of the feedstocks also allows for an early indication of such fraud, as UCO has far higher contents of the undesired nonmetal elements than virgin oils have. In this application note, the strategy for a quick and fully automated combined multi-element determination including total chlorine, total nitrogen, and total sulfur contents, in a very wide range starting from ultra-traces to upper ppm contents with the multi EA 5100 elemental analyzer is described.

Materials and Methods

Samples

- One "used" cooking oil sample, plant-based (oil-mix)
- One "fresh" vegetable oil (canola)
- One used animal fat (lard)

Reagents

- Kit calibration solutions, 0.1–10 mg/L S, (Analytik Jena GmbH+Co. KG, 402-889.070)
- Kit calibration solutions, 1.0–50 mg/L S, (Analytik Jena GmbH+Co. KG, 402-889.077)
- Kit calibration solutions, 100–500 mg/L S, (Analytik Jena GmbH+Co. KG, 402-889.164)

- Kit calibration solutions, 10–100 mg/L N, (Analytik Jena GmbH+Co. KG, 402-889.165)
- Kit calibration solutions, 100–500 mg/L N, (Analytik Jena GmbH+Co. KG, 402-889.162)
- Kit calibration solutions, 0.1–10 mg/L Cl, (Analytik Jena GmbH+Co. KG, 402-889.071)
- Kit calibration solutions, 10–100 mg/L Cl, (Analytik Jena GmbH+Co. KG, 402-889.166)
- o-xylene 99% (Thermo Fisher Scientific/Alpha Aesar, Art. No. A11358.AP), as solvent for dilution

Sample preparation

For N, S, and Cl determination the samples were diluted before analysis due to the expected high concentrations, increased viscosity, and partial inhomogeneity. For this purpose, the oils and the animal fat were homogenized by melting at 60 °C in a water bath first. An aliquot of these homogeneous samples was diluted mass-based (m/m) with o-xylene as a solvent. The dilution factors used ranged from 3 to 9, depending on the sample. The blank value of the diluent was determined and put into account for correction of the results. This strategy allows a fast processing of all samples together with one liquid sampler. Alternatively, a temperature-controlled autosampler can be used.

Calibration

Before analysis, the multi EA 5100 was calibrated. For this purpose, calibration solutions, in the concentration range from 0 to 100 mg/L, were used for nitrogen, sulfur, and chlorine. The used materials and selected calibration parameters are summarized in Table 1. An injection volume of 40 µL was used for the N, S calibrations and 100 µL for the Cl calibration.

The gained calibrations have been verified with certified reference standards.

Table 1: Calibration parameters for sulfur (S), nitrogen (N), and chlorine (Cl)

Parameter	Standard	Calibrated range	Correlation coefficient
TS	Dibenzothiophene in iso octane	0.04–0.4 µg S	0.99987
TN	Pyridine in iso octane	0.20–4.0 µg N	0.99999
TCI	2,4,6-Trichlorophenol in iso octane	0.01–5 µg Cl	0.99998

In figures 1 to 3, calibration curves for nitrogen, sulfur, and chlorine trace range are shown exemplarily.

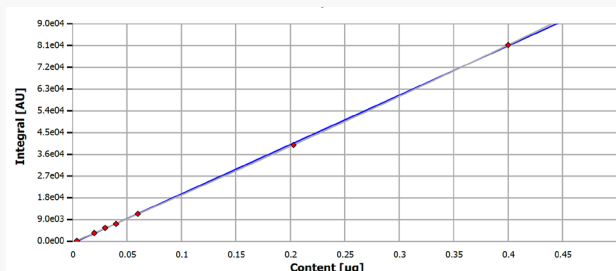


Figure 1: Sulfur calibration, trace range

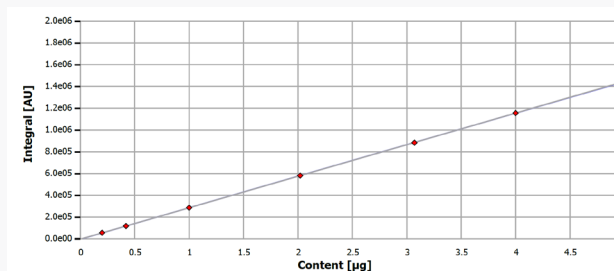


Figure 2: Nitrogen calibration, trace range

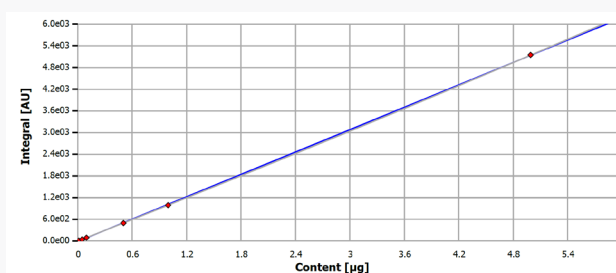


Figure 3: Chlorine calibration, trace range

Instrument settings

For the analysis, a multi-element analyzer type multi EA 5100 was used in horizontal operation mode. A UV-fluorescence detector (UVFD) was used for the determination of sulfur, a chemiluminescence detector (CLD) for the determination of nitrogen, and for the determination of chlorine, coulometric titration using the high sensitive

cell option was applied. The achievable detection limits of the measuring system used are 50 µg/L Cl, 5 µg/L S, and 10 µg/L N.

For automated sample introduction and transfer into the combustion furnace, the system was equipped with an automatic boat drive (ABD) with flame sensor and a

multi-matrix sampler (MMS). The flame sensor ensures safe and quantitative combustion of each sample matrix within the shortest possible measurement time. This eliminates the need for time-consuming method development and creation of boat programs for each sample type. This makes analysis simple and reproducible, eliminates sources of error, and reduces maintenance compared to classic boat programs. For the measurements, a defined sample volume was dosed into a quartz sample boat, placed in the automatic boat drive using the μL -syringe of the MMS. Afterwards, the boat is automatically transferred to the combustion furnace, controlled by the flame sensor. The flame sensor adapts the process to the special requirements of the respective sample component, ensuring matrix-independent results. Sample digestion was carried out by efficient catalyst-free high-temperature combustion. The process is divided

into two phases. In the first phase, the volatile sample components are vaporized in an inert gas stream, followed by combustion of the gaseous products formed in an oxygen-rich atmosphere. In the second phase, the heavier, non-volatile sample components and the pyrolysis products formed are quantitatively oxidized in pure oxygen. The formed gaseous reaction products SO_2 , NO_x , and HX are transferred to the respective detection systems after complete drying. The Auto-Protection system guarantees highest operational safety and efficient protection. Particles and aerosols are retained, only the analyte gas can pass. Switching between simultaneous N/S analysis and coulometric chlorine detection is done quickly and fully automatically without manual conversion by this assembly.

Method parameters

A multi-element method from the method library was used for the analysis of the standards and samples. The parameters for combustion and detection are summarized in Tables 2 and 3. The injection volume for the N, and S determination was 40 μL . For chlorine determination a volume of 100 μL was used.

Table 2: Process parameters multi EA 5100 – horizontal mode

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 combustion)	200 mL/min
Sample: draw-up	2.0 $\mu\text{L}/\text{s}$
Sample: inject	2.0 $\mu\text{L}/\text{s}$
ABD mode	automatic*

* Flame sensor controlled, automatically optimized combustion

Table 3: Detection parameter for chlorine (high sensitive cell), sulfur (UVFD), and nitrogen (CLD) determination

Parameter	Setting		
	Chlorine	Sulfur	Nitrogen
Max. integration time	1200 s	700 s	700 s
Cell temperature	22 °C	-	-
Titration delay	1	-	-
Start	-	0.2 ppm	0.5 ppm
Threshold	300 cts	0.2 ppm	0.5 ppm
Stability	-	7	7
Threshold value	25 cts	-	-
Baseline / drift correction	automatic	-	-

Results and Discussion

The results for the simultaneous N/S, and sequential CI determinations of the control standards and different sample types are summarized in Table 4. These are mean values from triplicate determinations. The high efficiency of combustion and sample introduction are reflected in the excellent reproducibility and low scatter of the measurement results, which is mainly below 3%.

Table 4: Results of the multi-element analyses for samples and standards

Sample	$c_s \pm SD$ [mg/L]	RSD [%]	$c_N \pm SD$ [mg/L]	RSD [%]	$c_{CI} \pm SD$ [mg/L]	RSD [%]
Cooking oil (fresh)	3.50 ± 0.09	2.57	26.0 ± 0.02	0.08	0.37 ± 0.01	0.03
Cooking oil (used)	5.51 ± 0.14	2.54	49.2 ± 0.10	0.02	11.4 ± 0.23	2.02
Frying fat (animal based)	57.2 ± 1.40	2.45	497 ± 1.00	0.20	10.6 ± 0.35	3.00
Standard 10.0 mg/L CI	-	-	-	-	10.1 ± 0.01	0.10
Standard 50.0 mg/L N and S	50.0 ± 0.18	0.36	49.6 ± 0.15	0.30	-	-
Standard 5.0 mg/L N and S	4.98 ± 0.14	2.76	5.00 ± 0.07	1.40	-	-

The figures 4 to 12 show representative N, S, and CI measurement curves for the control standards and diluted samples.

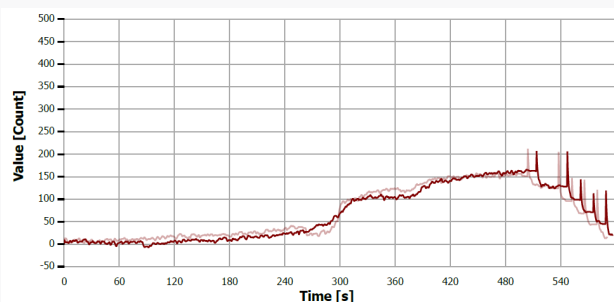


Figure 4: CI measurement curve for cooking oil (fresh)

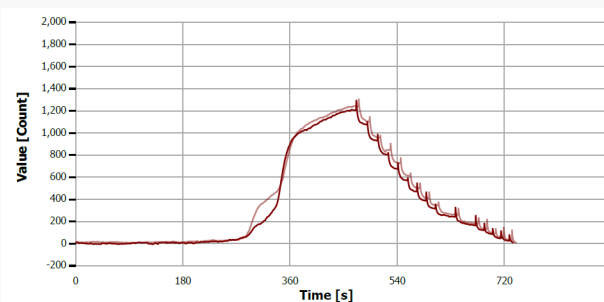


Figure 5: CI measurement curve for cooking oil (used)

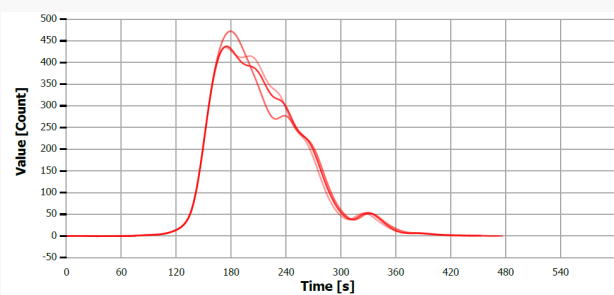


Figure 6: N measurement curve for cooking oil (fresh)

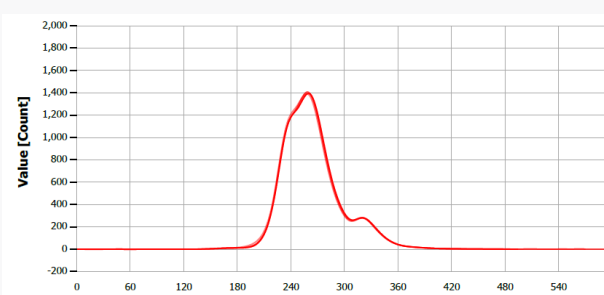


Figure 7: N measurement curve for cooking oil (used)

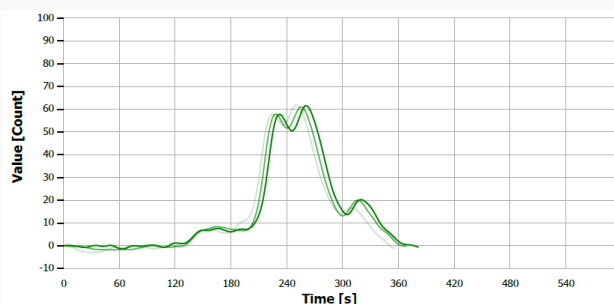


Figure 8: S measurement curve for cooking oil (fresh)

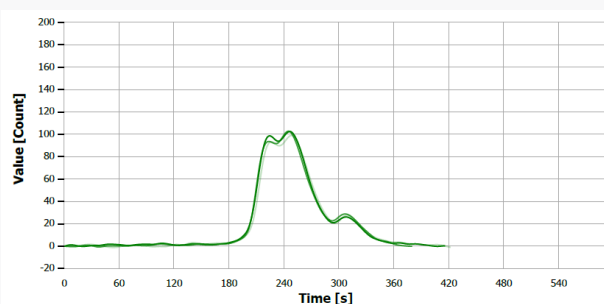


Figure 9: S measurement curve for cooking oil (used)

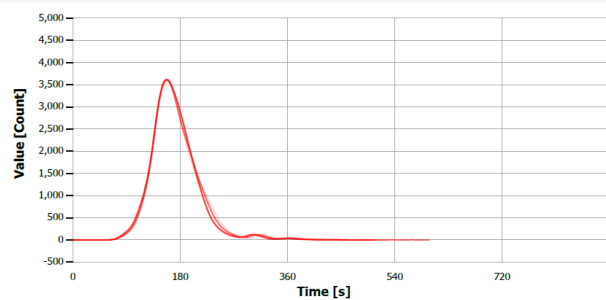


Figure 10: N measurement curve standard 50.0 mg/L

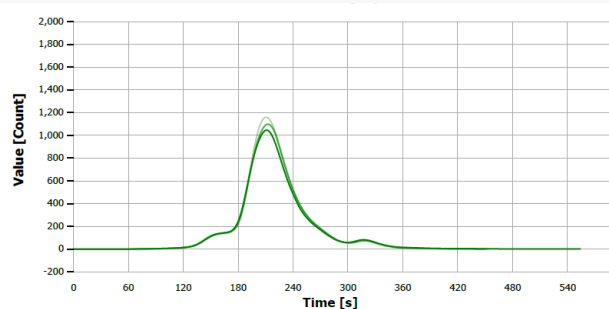


Figure 11: S measurement curve standard 5.00 mg/L

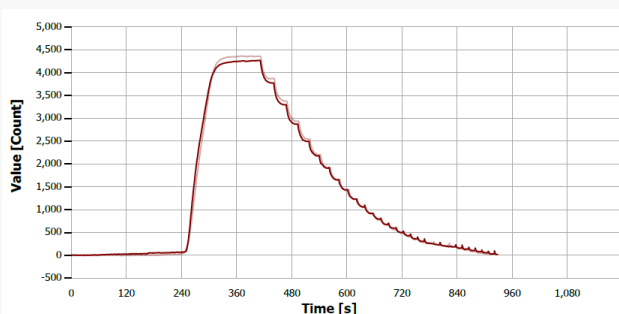


Figure 12: Cl measurement curve standard 10.0 mg/L

The shape of the measurement curves appears visually varying. This progress reflects the control behavior of the flame sensor to create optimum combustion conditions. When looking at the analysis results, however, the superb reproducibility of less than 3% RSD is an indicator for high repeatability and therefore reliable results.

Summary

The elemental analyzer multi EA 5100 offers a simple and reliable solution for precise and fast multi-element analysis in highly viscous matrices such as used cooking oils and fats. Sulfur and nitrogen contents are determined simultaneously. Chlorine is determined sequentially with the same analyzer, without any manual instrument modification. The HiPerSens detection provides lowest detection limits and a very wide linear measuring range for N, S, and Cl. This allows for the analysis of significantly contaminated used oils, process intermediates, but also the produced high-purity end products, the biofuels, with the same instrument and analysis method. This significantly saves time, especially for smaller companies who have to stringently monitor the entire production process – beginning with highly contaminated feedstocks up to ultra-pure final products, including the compliance with legal emission limits (e.g., 10 mg/L S Euro VI).

The flame sensor enables reliable, reproducible, and fast digestion of any sample matrix without method development, thus guaranteeing results in the shortest possible measuring time. The formation of soot or other



Figure 13: multi EA 5100 with ABD and MMS autosampler in liquids mode

undesirable pyrolysis products, the resulting increased maintenance effort, and incorrect analysis results are, thus, prevented from the outset.

If other analytical tasks come into focus, e.g., analysis of carbon or TOC in process or wastewater, the analyzer can be extended easily with a suitable accessory module.

Recommended device configuration

Table 5: Overview of devices and accessories

Article	Article number	Description
multi EA 5100	450-300.011	Basic module with combustion
N module	450-300.022	Chemoluminescence detector for nitrogen
S module basic	450-300.021	UV fluorescence detector for sulfur
Cl module	450-300.023	Module for determination of chlorine contents by coulometric titration
Extension kit Cl "high sensitive"	450-300.024	Extension for chlorine determination in the trace range
Automatic Boat Drive - ABD	450-300.013	Automatic boat drive with flame sensor technology – sample supply in horizontal mode
Multi Matrix Sampler - MMS	450-300.030	Sampler for automatic dosing of liquids, solids, AOX, EOX and TOC samples
Liquids kit for MMS 5100	450-300.033	Accessory for the dosing of liquid samples
multiWin software	450-011.803	Control and data evaluation software

References

- [1] Used Cooking Oil Market Insights [2023-2030] | The Definitive Industry Guide, <https://www.linkedin.com/pulse/used-cooking-oil-market-insights-2023-2030-definitive/>
- [2] ICCT, 2022. WORKING PAPER 2022-13 - An estimate of current collection and potential collection of used, International Council on Clean Transportation. United States of America. Retrieved from <https://policycommons.net/artifacts/4820393/working-paper-2022-13/5656949/> on 05 Dec 2023. CID: 20.500.12592/d9w5tj.

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Headquarters

Analytik Jena GmbH+Co. KG Phone +49 3641 77 70 info@analytik-jena.com
 Konrad-Zuse-Strasse 1 Fax +49 3641 77 9279 www.analytik-jena.com
 07745 Jena · Germany

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