



### Challenge

Quick, automated, and accurate total chlorine determination in highly viscous oil without prior sample treatment or dilution.

### Solution

Temperature controlled sample supply and automatic adaptation of combustion process by intelligent sensor technology.

### Intended audience

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

## Fully Automated Determination of Total Chlorine Contents in Different Edible Oils by means of Combustion Elemental Analysis and Coulometric Titration

### Introduction

In 2022 alone, more than 220 million tons of edible oils were produced worldwide. Whether for food preparation, in the production of processed foods, or for cosmetics, biofuels, oleochemicals and pharmaceuticals - edible oils are irreplaceable. To protect consumers and the environment, standards and guidelines ensure the continuous monitoring of 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 large sample volumes in the shortest possible time. In addition to metal and heavy metal traces, nonmetals such as sulfur, nitrogen, and chlorine often need to be determined. Especially chlorine is not a natural component

of edible oils, but enters the product as an impurity. It can affect the production process and the quality and properties of the final product such as odor, color, taste, and shelf life. Testing for chlorine is necessary not only for quality but also for safety reasons. One example is inorganically bound chlorine, which is suspected of contributing to the formation of the carcinogenic 2- and 3-monochloropropane-1,2-diol (3-MCPD, 2-MCPD). Such compounds can enter edible oils and eventually foods in many stages of the value chain. 3-MCPD is formed when fats and oils are exposed to high temperatures in the presence of organically and inorganically bound chlorine.

The World Health Organization has therefore set a limit of 2 µg/kg body weight for the daily intake of 3-MCPD. The formation of chlorine compounds must therefore be

constantly monitored in the refinery process.

In quality control of the products, chromatographic methods are often used to control 3-MCPDs. These procedures, though very precise, require time-consuming sample preparation and method optimization. During process monitoring, however, quick response is required when taking action to prevent the formation of 3-MCPD.

A technique that detects all Cl compounds is more suitable here. Combustion elemental analysis is such a technique. It

is becoming increasingly popular in process monitoring in oil mills and refineries. The method is established and described in detail in a variety of relevant international regulations such as ASTM D4929-B, ASTM D5808, UOP 779. This application note gives you insights how to quantify chlorine as a sum parameter (TX) with little effort, and how to make process monitoring in edible oil production efficient and safe.

## Materials and Methods

### Samples and Reagents

- 14 edible oil samples taken from different stages of the production process (feedstock, intermediates, final products) resp. different production approaches (cold-pressed, solvent extracted, refined, hydrogenated), and one ultra-pure reference oil (paraffine oil)
- Kit calibration solutions, concentration: 0.1 – 10 mg/L Cl, Analytik Jena GmbH+Co.KG, 402-889.071
- Kit calibration solutions, concentration: 10 – 100 mg/L Cl, Analytik Jena GmbH+Co.KG, 402-889.166

### Sample Preparation

Samples and standards were analyzed directly without sample pretreatment. The sample matrices provide a representative spectrum from the range of edible oils derived from plant seeds. Due to their main components - long-chain hydrocarbons, so-called fatty acids - their viscosity is high. To avoid pretreatment of the samples, a heated sample supply system was used. A temperature-controlled liquid sampler allows direct injection with a syringe. For homogeneous liquids with high viscosity, heating to 75 °C significantly reduces the viscosity. Another approach is to dilute the samples with a suitable solvent to reduce viscosity and allow automated sample injection without a dedicated sampler. In the following use case, the first approach will be applied.

### Calibration

Prior to sample measurement, the multi EA 5100 was calibrated for chlorine determination. Liquid standards based on 2,4,6-trichlorophenol (Cl) in isooctane with a concentration range from 0.1 up to 100 mg/L Cl were used. The obtained calibration was verified with certified reference standards. An injection volume of 100 µL was applied for the calibration and verification measurements. Figure 1 shows an example Cl calibration curve in the ultra-trace range. The related performance data are listed in table 1.

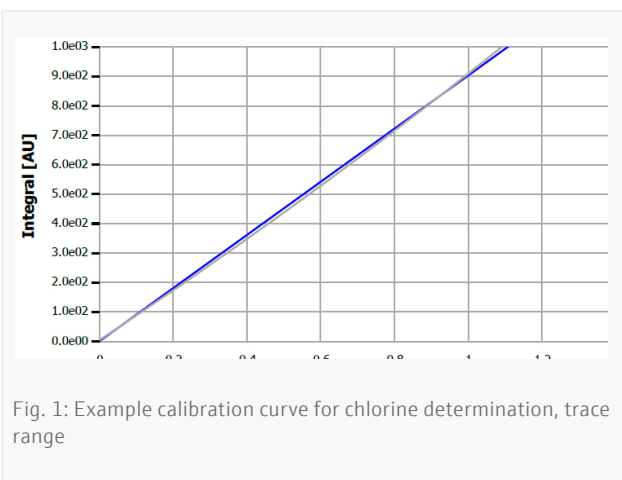


Fig. 1: Example calibration curve for chlorine determination, trace range

Table 1: Chlorine calibration – performance parameters

Parameter	Value
Injection volume	100 µL
Range	0 – 1.0 µg
Detection limit	19.96 µg/L
Linearity	linear
Correlation coefficient	1.00000

## Instrumentation

A multi EA 5100 analyzer equipped with a HiPerSens chlorine detector was used in horizontal operation mode. Automated sample introduction and transfer into the analyzer was carried out 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 highly viscous homogeneous liquids without prior dilution. The flame sensor ensures trouble-free and matrix-optimized transfer and combustion of the different sample materials. For chlorine determination, an injection volume of 100  $\mu\text{L}$  was used. Sample digestion was carried out by efficient catalyst-free high temperature combustion in a quartz tube. 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, optimum 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

## Method Parameters

A standard library method was used for the analysis of the liquid standards and the oil samples. The method and evaluation parameters are summarized in table 2. The injection volume for the Cl determination was set at 100  $\mu\text{L}$ . A temperature-controlled syringe was used for direct injection of the undiluted samples. Both the syringe and the sample tray were kept at a constant temperature of 75  $^{\circ}\text{C}$  throughout the analysis period. This allows direct injection even for samples with high initial viscosity, thus avoiding time-consuming and error-prone dilution steps.

## Evaluation Parameters

The evaluation parameters for the detection of chlorine contents (TCl) by micro-coulometric titration are summarized in table 3.

formed gaseous products in an oxygen-rich atmosphere. In the second phase, the heavier, non-volatile sample components and formed pyrolysis products are quantitatively oxidized in pure oxygen. Here, the flame sensor ensures the evaporation of the exact sample amount that can be completely oxidized by the available amount of oxygen. For this purpose, the resulting combustion flame is monitored in real-time. This allows for fully automatically adjusting the process to the specific requirements of the individual components.

The formed reaction gases are dried and transferred to the titration cell, where the formed HX is absorbed by the cell electrolyte. The chlorine is quantified by micro-coulometric titration with the "high sensitive" module. The implemented auto protection system, consisting of particle and aerosol trap, and a heated transfer line guarantee the complete transfer of the formed HX gas, without condensation loss. With this configuration a detection limit as low as 10 ng Cl absolute can be achieved.

Table 2: Process parameters multi EA 5100 - horizontal operation

Parameter	Setting
Furnace temperature	1050 $^{\circ}\text{C}$
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	2.0 $\mu\text{L/s}$
Injection speed	2.0 $\mu\text{L/s}$
ABD mode	Automatic*

\* flame sensor controlled automatically optimized combustion

Table 3: Detection parameters for Cl ("high sensitive" option)

Parameter	Setting
Max. integration time	1200 s
Cell temperature	22 $^{\circ}\text{C}$
Titration delay	1
Threshold	300 cts
Threshold value	25 cts
Baseline / drift correction	Automatic

## 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 memory effect was detected, which could have been caused by the higher viscosity of the samples. Low RSD values of the sample measurement were comparable to the measured values of the standard solutions and confirm the high reproducibility. Even for samples like canola oil, in which chlorine impurities occur only in the ultra-trace range, the quality of results was sufficient. This confirms 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 (used cooking oil), tall oil, cod liver oil or glycerol. In the following typical measurement curves for selected oil samples and standard solutions are shown. The chlorine content determined in the edible oil samples, except for the pumpkin oil, are as low as expected for refined oils used for food production, and do not indicate an increased risk for 3-MCPD formation. Only the pumpkin oil with its 27.7 mg/L Cl is conspicuous. Even though higher chlorine content can result from harmless natural compounds like vitamin B1 - as it is the case with pumpkin seeds - further assessment of the present chlorine compounds by chromatographic techniques is required.

Table 4: Results of total chlorine determination for the edible oil samples and standards

Sample	$C_{Cl}$ [mg/L]	$\pm$ RSD [%]
Rapeseed (canola) oil**	0.09	0.66
Olive oil	0.15	0.62
Mustard oil, native**	0.16	5.64
Mustard oil*	0.49	0.46
Mustard oil 2	1.06	2.14
Peanut oil	0.33	4.58
Linseed oil	0.71	2.41
Rice bran oil	0.78	2.93
Thistle oil	0.93	2.38
Soy oil	1.00	2.42
Corn oil	1.07	2.32
Sesame oil	2.60	2.03
Pumpkin oil	27.7	0.57
Paraffin oil SA	0.05	3.30
Standard 10.0 mg/L Cl	10.0	2.44
Standard 1.01 mg/L Cl	1.02	1.84

\* refined

\*\* cold-pressed

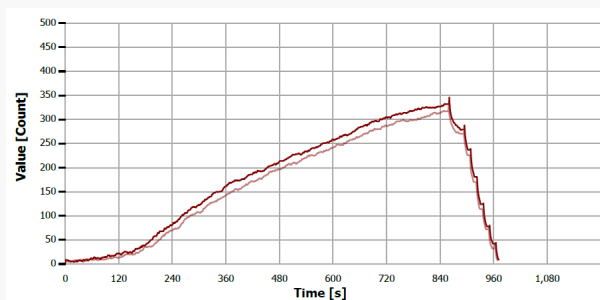


Fig. 2: TCL analysis curve, sample "linseed oil"

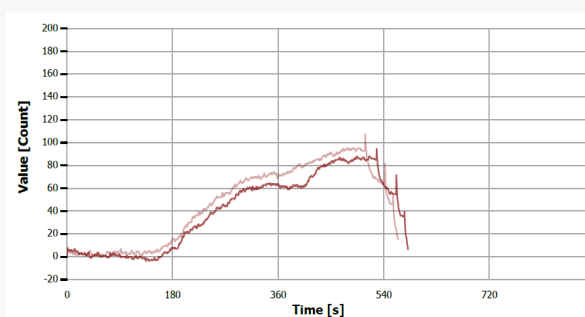


Fig. 3: TCL curve, sample "mustard oil, native"

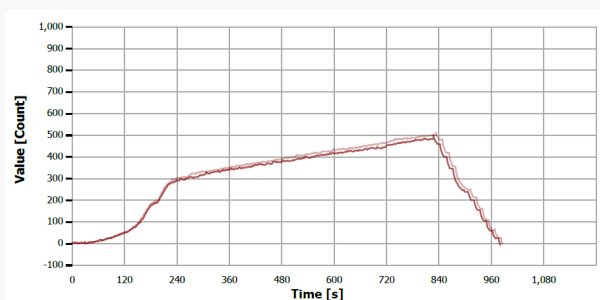


Fig. 4: TCL analysis curve, sample "mustard oil 2"

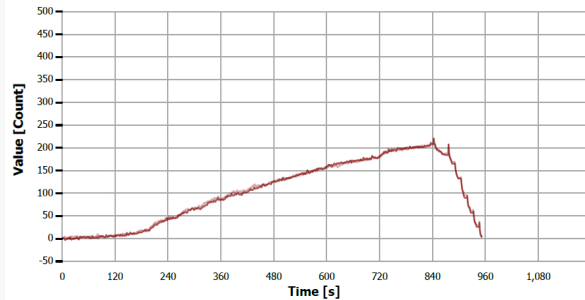


Fig. 5: TCL analysis curve, sample "mustard oil"

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

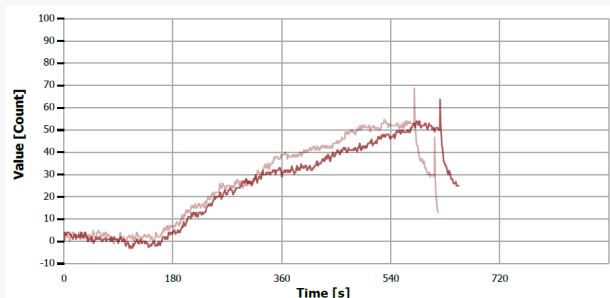


Fig. 6: TCL analysis curve, sample "rapeseed oil"

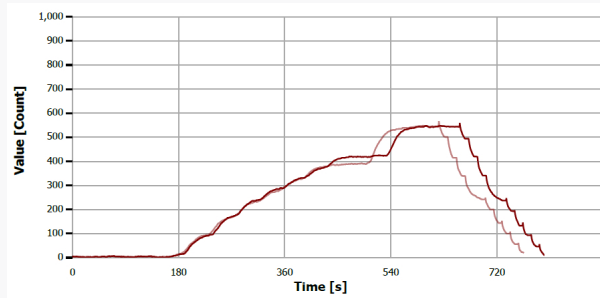


Fig. 7: TCL analysis curve, sample "corn oil"

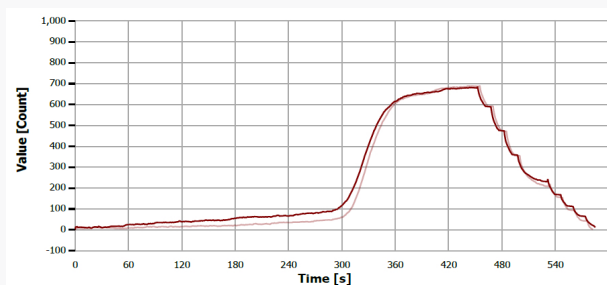


Fig. 8: TCL analysis curve, sample "sesame oil"

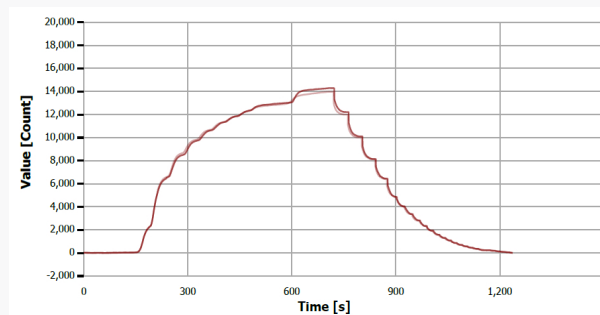


Fig. 9: TCL analysis curve, sample "pumpkin oil"

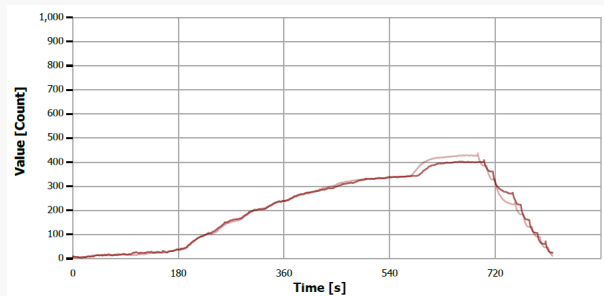


Fig. 10: TCL analysis curve, sample "rice bran oil"

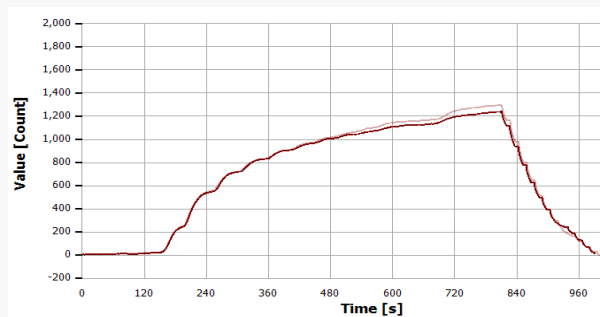


Fig.11: TCL curve, sample "thistle oil"

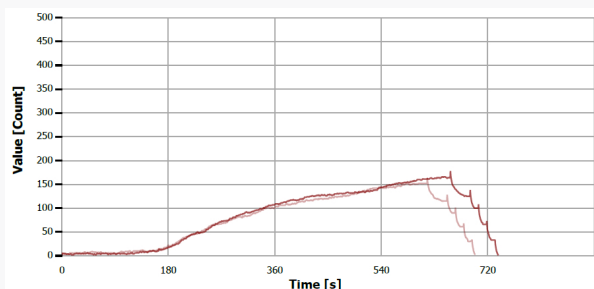


Fig. 12: TCL analysis curve, sample "peanut oil"

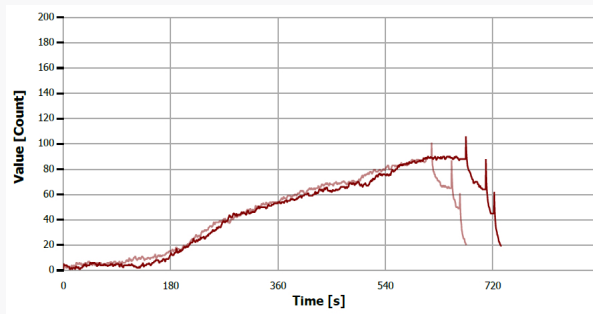


Fig. 13: TCL analysis curve, sample "olive oil"

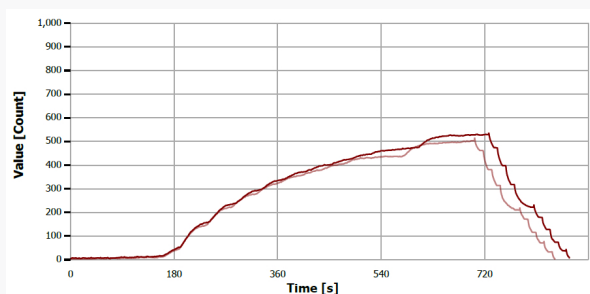


Fig. 14: TCl analysis curve, sample "soy oil"

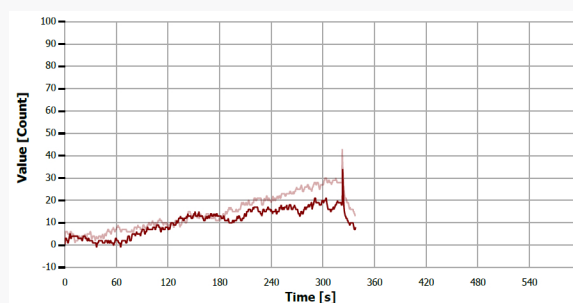


Fig. 15: TCl analysis curve, sample "white oil (paraffine)"

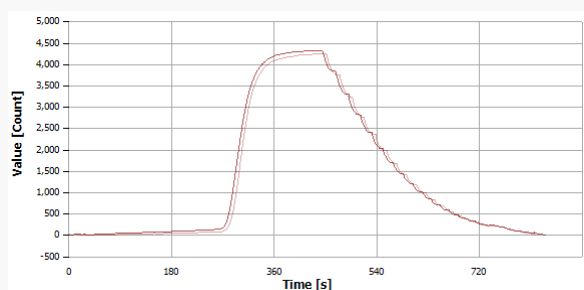


Fig. 16: TCl analysis curve, standard "10 mg/L Cl"

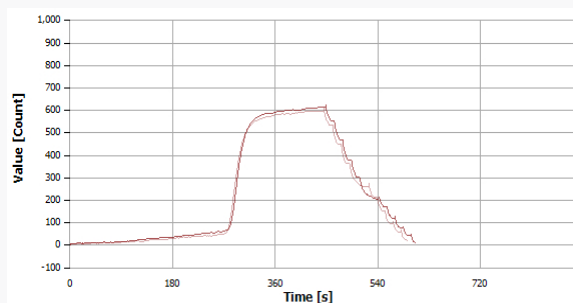


Fig. 17: TCl analysis curve, standard "1.01 mg/L Cl"

## Summary

The analyses were carried out using a multi EA 5100 with MMS-T in horizontal mode, which enables direct, time-optimized analysis of viscous sample matrices, such as edible oils. Thanks to the efficient heating of the sample tray and dosing syringe of the liquid autosampler, viscous matrices were injected without a subsequent dilution step. This saves valuable working time and money, reduces solvent consumption and avoids the risk of user errors. This ensures reliable results, especially for determining very low element contents close to the detection limit. The flame sensor-based, fully automated optimization of the combustion process creates ideal digestion conditions for any organic matrix and avoids incomplete combustion and system contamination without the need for manual adjustments or special digestion programs. A single method is sufficient to analyze the full range of liquid matrices, regardless of viscosity, volatility, combustibility, and concentration. This eliminates the need for matrix-specific method development and ensures the best comparability of results. If required, the application range of the analyzer can be easily extended by accessory modules for the determination of nitrogen, sulfur, and/or carbon contents.



Abb. 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	Elemental analyzer for the determination of total sulfur, nitrogen, chlorine, and carbon in solids, liquids, and gases
Cl module	450-300.023	Extension of multi EA 5100 for chlorine determination with coulometric titration
Extension kit Cl high sensitive	450-300.024	Extension of multi EA 5100 Cl module basic, for determining very low chlorine contents in solids, liquids, and gases
ABD	450-300.013	Automatic boat drive with flame sensor technology - horizontal operation of multi EA 5100
MMS-T	450-900.453	Temperature-controlled autosampler with heating and cooling option for liquids, extendable for solids analysis
multiWin software	450-011.803	Operation and data evaluation software for multi EA 5100

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