Challenge

Fully automated, fast and accurate determination of different chlorine parameters (TCl, TICl, TOCl) in different types of palm oil

Solution

Organic Elemental Analysis - Matrix- and time optimized combustion with flame sensor technology using the multi EA 5100

Determination of Different Chlorine Parameters in Palm Oil

Introduction

Palm oil and palm kernel oil production has grown drastically in the last 50 years. With more than 30%, it is the largest contributor to global oil and fat production. Traditionally the food and cosmetics industries are amongst the main consumers with a share of 70% of the world palm oil production, followed by usage for biofuel production. Palm oil is used in products like margarine, oil, spreads, chocolate, cleaning agents, cosmetics, candles and many more.
To improve taste characteristics and shelf life palm oil needs to be refined. But refined palm oil can pose a health risk to consumers.
Various studies carried out during the last years have proven the presence of 3-monochloropropane-1,2-diol (3-MCPD) fatty acid ester in refined palm oil. 3-MCPD is formed when fats and oils are exposed to high temperatures, in the presence of organic and inorganic bound chlorine, which often happens during the refining process. 3-MCPD is suspected to raise the risk of cancer. Experiments have shown that higher uptake of 3-MCPD triggers kidney and liver damage and benign tumors. That is why the World Health Organization has set a threshold level for the tolerable daily intake of 3-MCPD at 2 µg/kg body weight.
Used as a food ingredient, palm oil is subject to strict quality and food safety controls. Besides the determination of antioxidants, water content or trace metals (Pb, As, Cd and Hg) also the determination of total chlorine plays an important role.

Perfectly suited for this purpose is the organic elemental analysis, coupling oxidative combustion and micro coulometric detection, a well-established technology widely used and described in industrial standards like ASTM D4929 method B, ASTM D5808 or UOP 779.

Materials and Methods

Samples and reagents

Different Cl standard solutions, palm oil samples and their dilutions with o-xylene have been analyzed.

- o-xylene (C_8H_{10}), puriss. p.a., (Riedel-de Haen, Art.-No.: 95662-1L)
- Isooctane (C_8H_{18}), Suprasolv®, GR for gas chromatography (Merck Art.-No.: 1.15440.1000)
- 2,4,6 trichlorophenol ($C_6H_3OCl_3$), GR for synthesis (Merck Art.-No.: 8.18469.0100)
- Calibration standard kit chlorine (0.1 – 10 mg/L) (Analytik Jena, Art.-No.: 402-889.071)
- Ultra-pure water

General sample preparation

Three different palm oil samples were analyzed. One crude palm oil, an intermediate from the production process and two final products of high quality and purity. One is a red palm oil, a viscous red-orange liquid used as high quality cold-pressed cooking oil, and the other one is a 100% natural palm kernel oil for cosmetics production, a white-ivory paste-like solid substance. Depending on the quality of raw material, production method and level of treatment, the homogeneity of palm oil samples differs, which has an effect on the reproducibility of results.
Due to the fact that the proportion of the chlorine-containing compounds in such matrices is also inhomogeneous, a sufficient pre-treatment strategy is crucial to ensure reliable measurement results.
That's why two different strategies were applied to prepare homogeneous sample aliquots. First, the samples were diluted 1:3 (w/w) with o-xylene. Second, they were carefully melted while gently shaking in a water bath, shortly before sampling. For this purpose, closed vials were used to avoid evaporation losses of the Cl-containing components. A third, very convenient type of "sample handling" is the use of an automatic sampler with integrated heating function for the sample tray and the dosing syringe. Here, the palm oil samples are tempered at slightly increased temperature, automatically by the system, so that dilution or external melting are not necessary. Thanks to the temperature-controlled dosing syringe, the sample can be dosed directly and reproducibly into the analyzer. The temperatures used can be flexibly adapted to the requirements of the respective sample.

Separation of inorganically-bound Chlorine

In some case it is very helpful to have additional information with regards to the type of Cl-compound. This helps to find possible sources of contamination and to better predict the risk potential of a palm oil during production process. Therefore, water-extraction is perfectly suited due to its simplicity and low effort. This method is recommended for low viscosity, non-asphaltene and non-bituminous crude materials. For effective extraction, especially when expecting high inorganic Cl load, a 3:1 water/sample ratio is recommended. Two different approaches are applicable for extraction of the palm oil samples.

Extraction by centrifugation

A 3:1 water/sample mix is prepared. Therefore, 25 mL of the crude sample are filled into a centrifuge vessel of suitable capacity, then 75 mL of approx. 60 °C warm ultra-pure water is added before the vessel is closed with a cap. This sample/water mix is shaken vigorously (~ 3,000 rpm) for two minutes by aid of a centrifuge. Periodically degassing the sample by venting the cap will prevent gas buildup. In case a heated centrifuge is used, the sample/water mix, is centrifuged with appropriate counterbalance, for ten minutes. This will effectively remove particulates and the inorganic chlorides from the organic phase (crude sample) into the water phase (water extract). After sufficient time for phase separation, aliquots of both phases are pipetted carefully for Cl analysis, making sure to take the sample from the middle of each phase without picking up contamination from the other phase.

Extraction by separatory funnel

25 mL of crude sample are filled into a separatory funnel, 75 mL of ~ 60 °C warm ultra-pure water is added. In the case of solvent-diluted crudes, 50 mL of the crude/solvent mix and 150 mL of ~ 60 °C warm ultra-pure water is used instead. The separatory funnel is capped before shaking it vigorously for two minutes. Periodically degassing the sample by venting the cap will prevent gas buildup. The sample/water mix needs approx. 10–15 minutes undisturbed for sufficient phase separation. The water sample is drained from the bottom of the separatory funnel for Cl analysis.
Independent of the extraction method used, it is important to make sure no particulates are present before analyzing the water extract. If necessary it can be filtered.

Instrumentation settings

A multi EA 5100 in horizontal operation mode, including the flame sensor technology, was used for the analysis.
For sample feeding the automatic boat drive in combination with the multi matrix sampler – MMS was used. In solids mode the undiluted samples were introduced directly by means of sample boats. In liquids mode 100 µL of the diluted samples resp. the liquid standards were injected by means of a µL-syringe.
The sample digestion is carried out by efficient catalyst-free high temperature combustion in a quartz reactor. This process is controlled and adopted to the special needs of every matrix component fully automatically thanks to 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, evaporation of light components and pyrolysis of the heavier ones takes place within an inert argon atmosphere. 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 (particle and aerosol trap) and a complete transfer (no condensation loss) of the formed HCl into the titration cell. Afterwards, the determination of the chlorine content is carried out by means of micro-coulometric titration. The multi EA 5100 enables a wide operation range from 10 wt-% down to the detection limit of 50 µg/L Cl.

Method parameters

Standard method settings for the horizontal operation mode are applied. The combustion process parameters are shown in Table 1 and the TCl detection parameters in Table 2.

Table 1: Process parameters

Parameter	Specification
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
Purge*	100 s
Draw up**	1 µL/s
Injection**	3 µL/s

Table 2: Detection parameters

Parameter	Specification
Max. integration time	1200 s
Threshold value	300 cts
Max. drift	100 cts/s
Threshold	25 cts
Cell temperature	23 °C
Titration delay	30 s

* for the solids method only, ** for the liquids method only

Calibration

Liquid calibration standards based on 2,4,6-trichlorphenol in isooctane were used to calibrate the analysis system in the concentration range from 0.1 to 5 mg/L TCl. The calibration curve is shown in Figure 1. The calibration was checked with a certified reference standard.

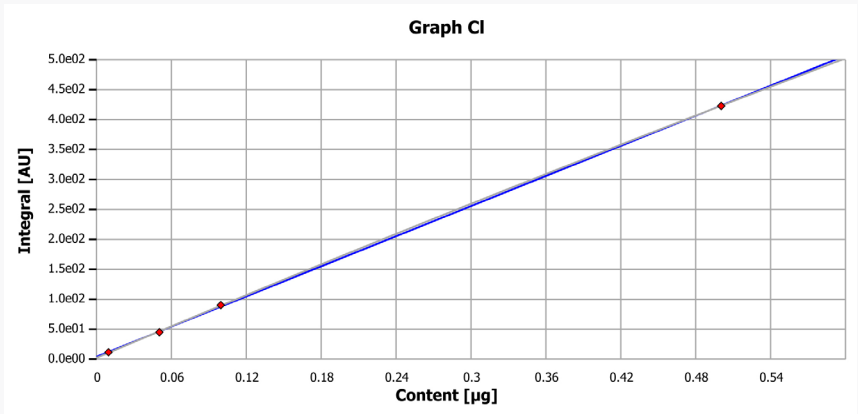

Fig. 1: Calibration curve for the TCl determination

Results and Discussion

The two different palm oil samples were analyzed two times – first directly, using the solids mode, and second in liquids mode, diluted with o-xylene. The results and the measurements of two selected Cl standards are summarized in Tables 3 (undiluted) and 4 (diluted). The results are averages of three replicate analyses. Typical measuring curves are shown in Figures 2a-b (undiluted) and 3a-b (diluted).

Table 3: Results of TCl determination in undiluted palm oil using the solid method

Measurement	TCl	RSD	Sample quantity
red palm oil	1.27 mg/kg	± 5.95 %	~ 55 mg
white palm oil	3.03 mg/kg	± 25.7 %	~ 25 mg
TCl standard 1.45 mg/kg	1.49 mg/kg	± 0.29%	100 µL

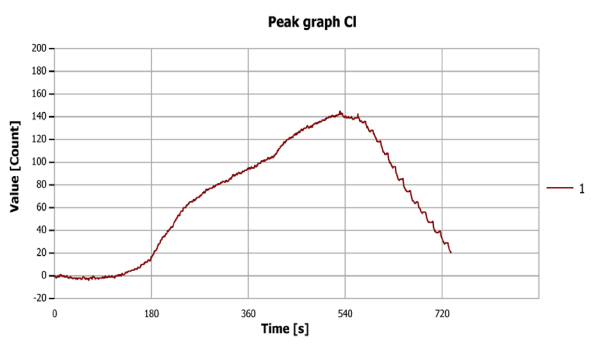

Fig. 2a: TCl measuring curve for the undiluted red palm oil

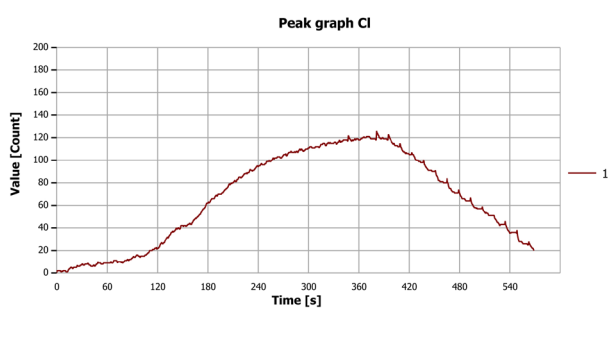

Fig. 2b: TCl measuring curve for the undiluted white palm oil

Table 4: Results of TCl determination in diluted palm oil samples

Measurement	TCl	RSD	Dilution [g in g]
red palm oil	1.30 mg/kg	± 1.99 %	3.5559 in 7.3622
white palm oil	3.16 mg/kg	± 2.91 %	3.4382 in 8.1002
TCl standard 0.72 mg/kg	0.71 mg/kg	± 0.54 %	-

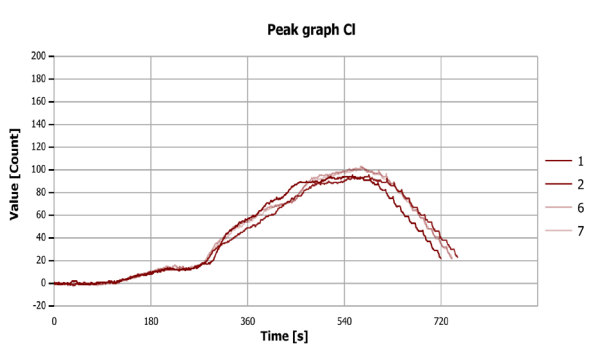

Fig. 3a: TCl measuring curves for diluted red palm oil

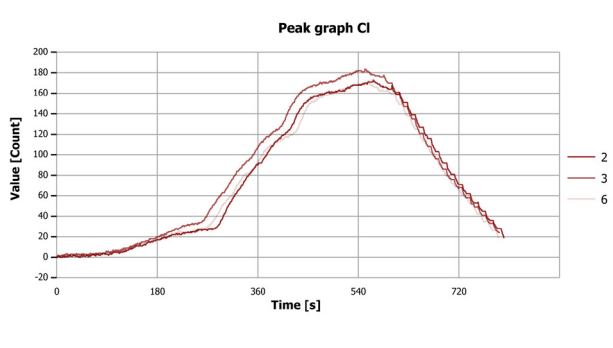

Fig. 3b: TCl measuring curves for diluted white palm oil

The different pre-treatment strategies deliver comparable results with deviations of less than 5%, thus demonstrating the general suitability of both principles for analysis of diverse palm oil samples.
Nonetheless, using dilution leads to smaller deviations of the single analyses. This as well as the easier sample handling and faster processing make the dilution strategy the superior one.

Speciation of inorganic and organically bound Chlorine

In some cases it is very helpful to have additional information with regards to the type of Cl-compound. This helps to find possible sources of contamination and to better predict the risk potential of a palm oil during processing.
The way to do this - a water extraction - is well established for oils and other not water-soluble organic samples.
In this study, the samples have been extracted manually before determination of total inorganic-bound chlorine (TICl). Therefore, the separatory funnel method was applied. The water extracts thus prepared are analyzed quickly by aid of a cell direct method, that means direct injection of the water extract into the titration cell. This only gives result for ionic chlorine, no falsification by soluble organic matter.

Depending on the analytical task, the organically bound Cl (TOCl) can either be calculated from the known TCl content or measured from the organic phase via combustion followed by coulometric titration.

For the crude palm oil sample, the total chlorine content as well as its proportions of inorganic and organically bound chlorine were measured directly. The results are summarized in Table 5, they are average values of three replicate analyses.

Table 5: Results for the determination of chlorine species in crude palm oil

Parameter	Concentration	RSD
TICl	10.6 mg/kg	± 0.72%
TOCl	1.22 mg/kg	± 2.68%
TCl	11.8 mg/kg	± 0.92%

The calculated (TICl + TOCl) and the measured TCl are equivalent. This aproves the reliability of both measuring methods.

Conclusion

This work has successfully demonstrated that the multi EA 5100 with ABD and flame sensor technology provides a fast, safe and reliable solution for the analysis of Cl traces in palm oil and related matrices. Due to the time- and matrix-optimized digestion process by means of the flame sensor, the quantitative combustion of any sample component is ensured. No formation of soot or other undesired pyrolysis products is observed. This and the efficient Auto-Protection system enable superior reproducibility even for the smallest chlorine quantities. A high sample throughput is easily achieved using the multi-matrix sampler MMS that is able to introduce solid as well as liquid sample matrices fully automatically either by quartz boats or by direct syringe injection.

Thanks to the modular design of the multi EA 5100 the user has any flexibility for later upgrades to determine other parameters like Nitrogen, Sulfur or Carbon in different matrices like LPG and gases.

References

[1] EFSA CONTAM Panel (EFSA Panel on Contaminants in the Food Chain); SCIENTIFIC OPINION ON THE RISKS FOR HUMAN HEALTH RELATED TO THE PRESENCE OF 3- AND 2-MONOCHLOROPROPANE-DIOL (MCPD), AND THEIR FATTY ACID ESTERS, AND GLYCIDYL FATTY ACID ESTERS IN FOOD. EFSA Journal. 2016, 14/5, 4426, 159

[2] Bertrand Matthäus, ORGANIC OR NOT ORGANIC – THAT IS THE QUESTION, Eur. J. Lipid Sci. Technol. 2012, 114, 1333–1334

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