APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Early Detection of Chloride in 3-MCPD Precursors in Palm Oil Through the Analysis of Chloride in Edible Oil with the Avio 200 ICP-OES

Introduction

During the production of palm oil, 3-MCPD (3-monocholorpropane-1,2-diol) forms from the reaction of acylglycerol with the chloride ion (Cl$^-$), as shown in Figure 1. 3-MCPD is a potentially carcinogenic compound, with a tolerable daily intake of 2 µg/kg of bodyweight.[1] As a result, the palm oil industry limits the 3-MCPD concentration to less than 10 mg/kg.

Because 3-MCPD only forms in the presence of Cl$^-$, removal of free Cl$^-$ is critical. Chloride is introduced from the raw palm fruit, which accumulates Cl$^-$ by uptake from the soil, water, and fertilizer. During the processing of the palm fruit, steam is introduced to remove as much Cl as possible. However, if all Cl is not removed, 3-MCPD can be formed in further refining steps. Therefore, after initial processing, the crude palm oil (CPO) must be monitored for chloride content. If the chloride content is high (typically > 2 ppm), it must be removed from the CPO by steam treatment prior to the final refining steps to produce food-grade palm oil.

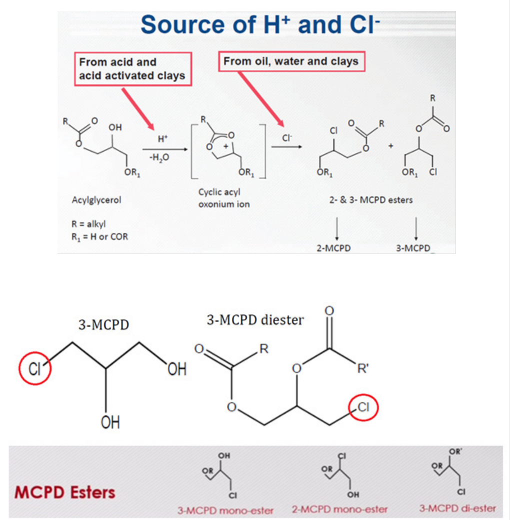

Figure 1. Formation and structure of 3-MCPD.

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Currently, the most common way to measure Cl in palm oil is to use a dedicated chloride analyzer, which performs an indirect measurement via titration, which involves either chloride reduction followed by sodium biphenyl titration or oxidative combustion followed by microcoulometric titration. Moreover, accuracy and reproducibility are dependent on the repeatable introduction of µL quantities of both the sample and titrant; any variation leads to poor reproducibility and accuracy.

As an alternative, PerkinElmer's Avio® 200 ICP-OES can be used to measure Cl with a simple liquid-liquid extraction. The Avio 200 hybrid-scanning system was chosen for this analysis for several reasons. First, the unique optical design of the Avio 200 results in unrivaled sensitivity for an ICP-OES instrument, which is important when measuring low-sensitivity analytes, such as Cl. The optical design also allows for simultaneous acquisition of all data points around the analyte peak at the same time as the analyte, resulting in stable, reproducible backgrounds, which translates into repeatable results. The use of Dynamic Wavelength Stabilization virtually eliminates wavelength drift by correcting for any residual spectral shifts to further increase the reproducibility of the results.

The Avio 200 ICP-OES is also a cost-effective solution, both in upfront cost and once it is put into production. The Avio 200 uses less than 9 L/min of argon during analysis, a direct result of the unique Flat Plate™ plasma technology design. The instrument can be completely powered down when not in use, saving electricity and gas costs. The fast startup of the Avio 200 means you can be analyzing samples in 10 minutes from a cold start, giving you the flexibility to analyze samples only when you have a need.

This work discusses the analysis of Cl in crude palm oil using the Avio 200 ICP-OES.

Experimental

Sample Preparation

Free chlorine was removed from the crude palm oil via a water extraction based on the procedure used in palm oil processing facilities to remove chlorine. The flowchart in Figure 2 summarizes the procedure. Since crude palm oil is a solid at room temperature, it was heated until it melted and turned into a liquid. A 50 g quantity of the melted palm oil was added to a 250 mL separation funnel, followed by 50 g of deionized water, which had been heated to 80-90 °C. The funnel was shaken 30 times, the phases were allowed to separate, and the aqueous phase was drained. The extraction was repeated by adding another 50 g of hot deionized water to the separation funnel, shaking, and draining as before, with the aqueous portions of both extractions being combined.

Pre-concentration was accomplished by evaporating the water on a hot plate to a final volume of about 5-10 mL. This solution was allowed to cool to room temperature and analyzed without any further sample preparation.

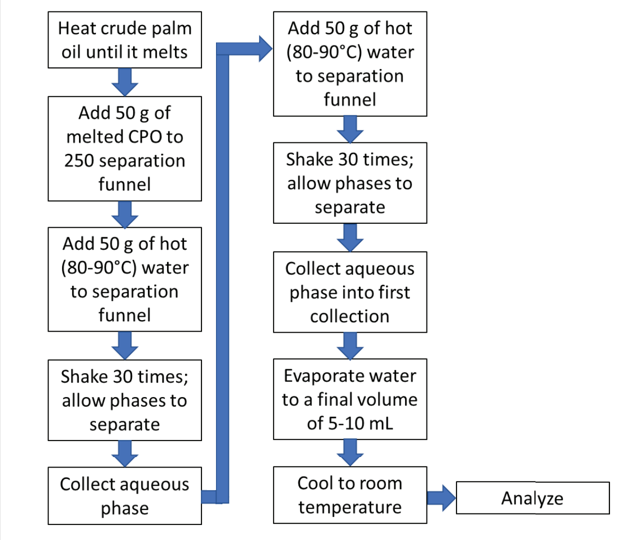


Figure 2. Sample preparation process for determination of chloride in crude palm oil.

All measurements were made against external standards prepared in deionized water using a linear calculated intercept algorithm. Calibration standards of 5, 10, 20, and 40 mg/L were prepared from dilution of a 1000 ppm Cl aqueous stock standard (Merck KGaA Darmstadt, Germany).

Instrumental Conditions

All analyses were carried out on the Avio 200 ICP-OES using the parameters shown in Table 1. Standard sample introduction parameters and components were used. The ability to monitor wavelengths higher than 800 nm, a unique capability of the Avio 200 ICP-OES, allowed Cl to be measured at 858.97 nm, a relatively sensitive wavelength for Cl.

Table 1. Avio 200 ICP-OES Instrumental Parameters for Determination of Cl.

Component/Parameter	Description/Value
Nebulizer	MEINHARD®
Spray Chamber	Baffled Cyclonic
Injector	2.0 mm Alumina
RF Power	1500 W
Sample Uptake Rate	1.0 mL/min
Nebulizer Flow	0.65 L/min
Auxiliary Flow	0.2 L/min
Plasma Flow	8.0 L/min
Plasma View	Axial
Torch Position	-5
Wavelength	858.597 nm
Processing Mode	Peak Area
Read Time	12 sec
Integration	0.12 sec
Replicates	3

Results and Discussion

The spectra of the calibration standards (5, 10, 20, 40 mg/L) at Cl 858.597 nm are shown in Figure 3, along with the resulting calibration curve in Figure 4. All calibration standards can clearly be seen above the blank and yield a linear regression greater than 0.9998.

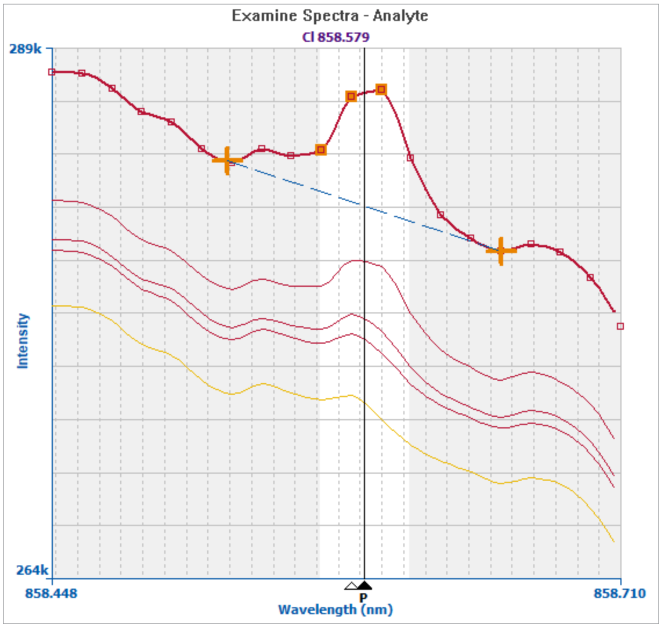
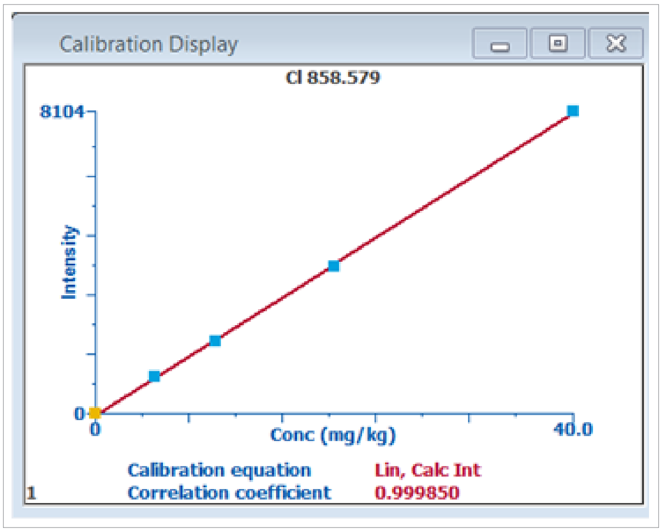


Figure 3. Spectra of calibration standards at Cl 858.597 nm.



Calibration equation Lin, Calc Int
Correlation coefficient 0.999850

Figure 4. Calibration curve for 5, 10, 20, and 40 mg/L Cl standards at 858.597 nm.

To determine the repeatability of the analysis, each calibration standard was measured three times as a sample against the calibration curve. The results appear in Table 2 and show recoveries within 10% of the true values for all concentrations, demonstrating the accuracy and reproducibility of the analysis.

Table 2. Measurement of Calibration Standards as Samples.

Cl Concentration (mg/L)	Average of Three Measurements (mg/L)	% Recovery
5	4.66	93
10	9.50	95
20	20.5	102
40	39.9	100

Spike recovery studies were performed by spiking 5 ppm Cl into the crude palm oil prior to the pre-concentration and extraction procedures. Both the spiked and unspiked samples were measured three times, with recoveries between 93-102% for each measurement (as shown in Table 3), demonstrating the accuracy of measuring low levels of Cl in palm oil.

Table 3. Cl Spike Recoveries in Crude Palm Oil

Sample	Unspiked (mg/L)	Spiked (mg/L)	% Recovery
1	2.24	7.68	109
2	2.22	7.55	107
3	2.48	7.54	101

To assess the lower limit of Cl detection in palm oil, method detection limits were determined by spiking palm oil with 2.5 ppm Cl and making seven consecutive measurements against the calibration curve. The standard deviation of the seven measurements was multiplied by 3.14 to give a detection limit of 0.06 ppm Cl in palm oil. The limit of quantitation (LOQ) was determined by multiplying the standard deviation by 10, which yielded an LOQ of 0.2 ppm – 50 times lower than the action level of 10 ppm established by the palm oil industry.

Conclusion

This work describes the determination of Cl in crude palm oil, an important analysis as Cl can react with other components during the production and refining processes to form 3-MCPD, a potentially carcinogenic compound. Sample preparation involved a simple liquid-liquid extraction which moves the Cl from the organic palm oil into an aqueous medium, where analysis was accomplished with the Avio 200 ICP-OES. The accuracy of the method was validated through calibrations and spike recoveries. Detection limits and the LOQ were significantly below the action levels used within the palm oil industry, allowing for increased confidence in the results.

Reference

1. MPOB Statement on 3-MCPD Esters https://pdf4pro.com/view/mpob-statement-on-3-mcpd-esters-36dba3.html

Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black (0.76 mm id), PVC, Flared	N0777043
Drain Tubing, Red/Red (1.14 mm id), PVC	09908585
15 mL Autosampler Tubes, Case of 500	B0193233

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