

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 220 Max ICP-OES

Introduction

During the production of palm oil, 3-MCPD (3-monochloropropane-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 $2 \mu\text{g/kg}$ 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 $> 2 \text{ ppm}$), it must be removed from the CPO by steam treatment prior to the final refining steps to produce food-grade palm oil.

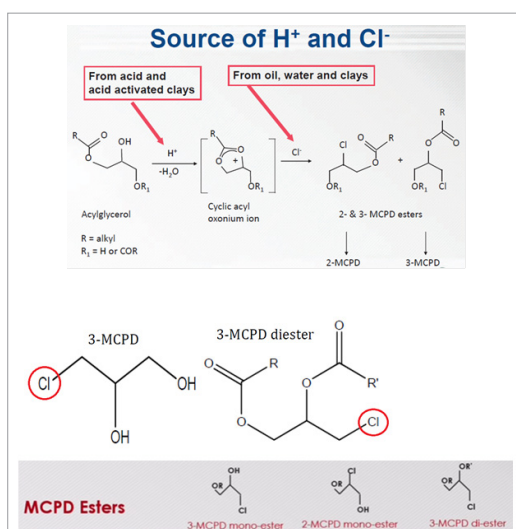


Figure 1. Formation and structure of 3-MCPD.

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® 220 Max ICP-OES can be used to measure Cl with a simple liquid-liquid extraction. The Avio 220 Max hybrid simultaneous system was chosen for this analysis for several reasons. First, the unique optical design of the Avio 220 Max 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 220 Max ICP-OES is also a cost-effective solution, both in upfront cost and once it is put into production. The Avio 220 Max 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 220 Max 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 220 Max hybrid simultaneous 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.

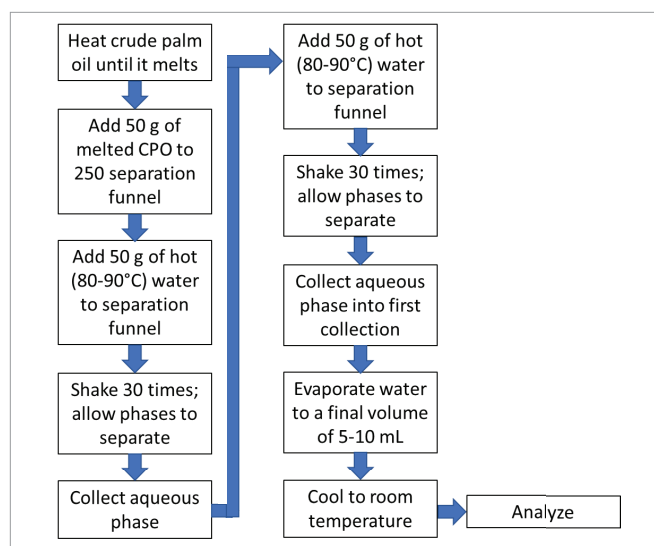


Figure 2. Sample preparation process for determination of chloride in crude palm oil.

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 220 Max 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 220 Max ICP-OES, allowed Cl to be measured at 858.579 nm, a relatively sensitive wavelength for Cl.

Table 1. Avio 220 Max 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 | 858.579 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 CI 858.579 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.

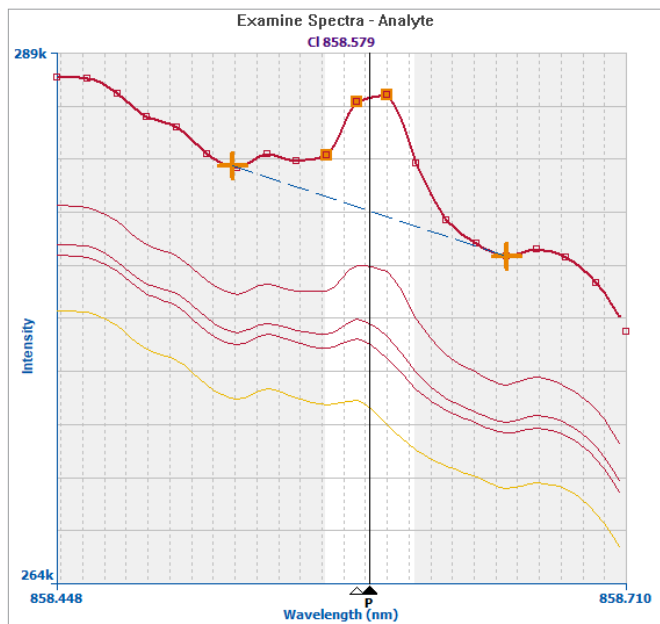


Figure 3. Spectra of calibration standards at CI 858.579 nm.

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.

| CI 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 CI 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 101-109% for each measurement (as shown in Table 3), demonstrating the accuracy of measuring low levels of CI in palm oil.

To assess the lower limit of CI detection in palm oil, method detection limits were determined by spiking palm oil with 2.5 ppm CI 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 CI 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 – 10 times lower than the action level of 2 ppm free chloride established by the palm oil industry.

Table 3. CI 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 |

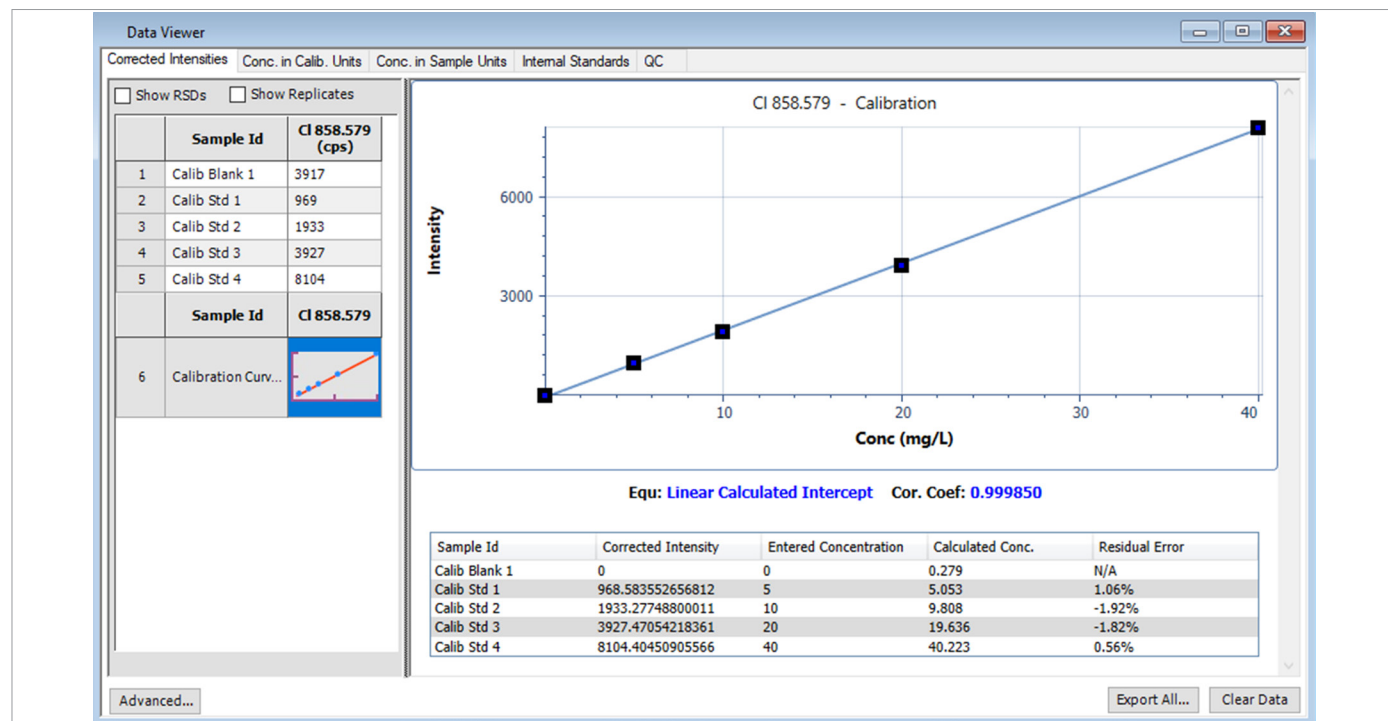


Figure 4. Calibration curve for 5, 10, 20, and 40 mg/L CI standards at 858.579 nm, as seen in Data Viewer's real-time results and Calibration window in Syngistix™ software.

Conclusion

This work describes the determination of CI in crude palm oil, an important analysis as CI 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 CI from the organic palm oil into an aqueous medium, where analysis was accomplished with the Avio 220 Max hybrid simultaneous 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 |