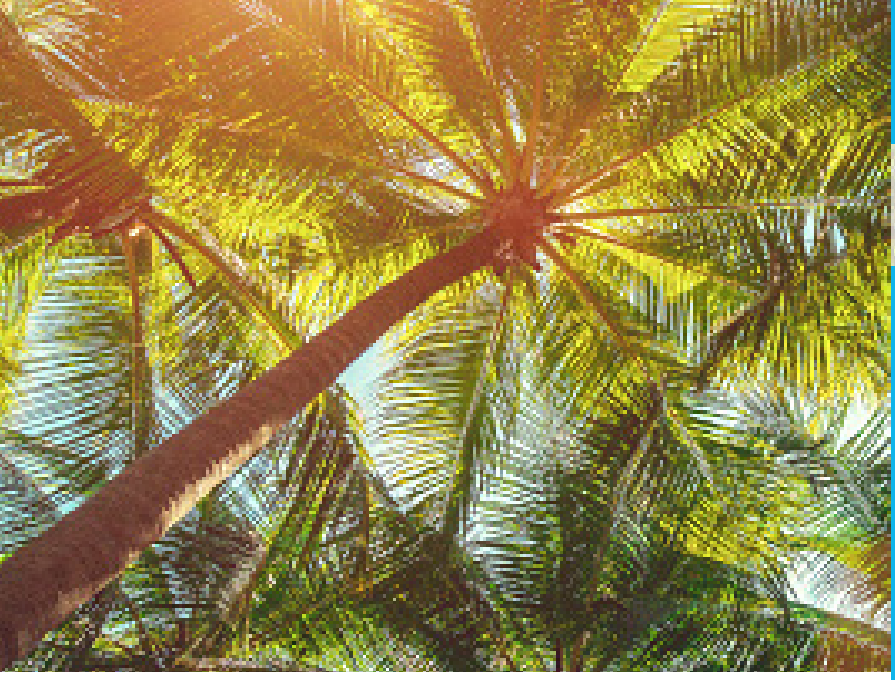

APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Determination of Total Chlorine in Palm Trees for Early Detection of 3-MCPD in Refined Oil Using the Avio 220 Max ICP-OES

Introduction

In recent years, the use and popularity of palm oil and its products have grown rapidly through its wide use in processed products like margarine, chocolate, cosmetics, candles and many others. However, due to the possible presence of 3-monochloropropane-1,2-diol (3-MCPD), the refined palm oil can have a potential health risk to the consumer. Europe, the US and Malaysia, the latter being one of the largest palm oil producers, have set limits for the maximum tolerable daily intake of 2 µg/kg 3-MCPD per body weight.[1] Therefore, in order to ensure food safety, the palm oil industry requires that the concentration of chlorine in the refined oil should be below 2 ppm, as chlorine (Cl) is the precursor for 3-MCPD formation.

3-MCPD is generated during the refinery process and is the product of the chemical reaction of acyl glycerol with organic and inorganic bound chloride at high temperatures. Monitoring the chlorine content during the whole palm oil production process plays an important role: the earlier chlorine is detected, the more effective the precautions can be taken to avoid the 3-MCPD formation in the refined palm oil. There are many ways to measure the chlorine, with titration being one of the most used methods. The advantage of titration is that it is easy to operate; however, because it is an indirect measurement, it is not as reproducible as direct measurement. In addition, titration is only a single-element analysis.

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One possible source of chlorine is the fresh fruit bunches which are harvested from palm trees. In this work, different parts of the palm tree were analyzed for Cl using PerkinElmer's Avio® 220 Max hybrid simultaneous ICP-OES, building off our previous work.[2] Compared to other available Cl analyzers, ICP-OES has the advantage of being a multi-purpose and multi-element technique. While Cl analyzers only perform indirect measurements of Cl, the Avio 220 Max ICP-OES provides a direct Cl measurement and can also be used to measure both major and micronutrients (i.e. P, K, Mg, Ca, Zn, B, Fe, Mn) in fertilizer, as well as the soil in palm plantations. In addition, ICP-OES can be used to continuously monitor the nutrients in different parts of the palm tree to decide on the frequency of fertilizing to ensure optimum yield at the plantation.

In palm refining, ICP-OES is used to monitor P, Fe, and Cu at different stages of the refining process to ensure the production of high-quality edible oil. Upstream processing produces oleochemicals used in many consumer products that must, therefore, be monitored for toxic elements (As, Cd, Hg, Pb, Sb), which can be accomplished with ICP-OES. As a result, the Avio 220 Max provides a better return on investment, compared to a dedicated Cl analyzer.

The Avio 220 Max hybrid simultaneous ICP-OES has a unique double-monochromator optical system with CCD detector, which provides excellent detection limits and wide wavelength range from 165-900 nm. The dual view plasma design enables the analysis of both trace and major elements in the same method. In addition, the Avio 220 Max ICP-OES also has the capabilities of fastest startup and low operating costs due to Dynamic Wavelength Stabilization and Flat Plate™ plasma technology.

Experimental

Sample Preparation

Four samples from different parts of the palm tree were analyzed:

- Palm leaf
- Empty fruit bunch
- Trunk
- Fronds

All these representative samples were digested using PerkinElmer's Titan MPS microwave digestion system. For each sample, 0.2 g was weighed into the Titan's standard digestion vessels, and then 9 mL nitric acid (concentrated) and 2 mL hydrogen peroxide (30%) were slowly added. The samples were pre-digested for 20 minutes before placing into the Titan MPS system. The digestion parameters used are shown in Table 1. After the digestion finished, the sample solutions were transferred into 50 mL polypropylene autosampler tubes and made up to 50 mL with DI water for analysis. All samples yielded clear solutions, indicating complete digests.

Step	Temp (°C)	Pressure Limit (Bar)	Ramp Time (Min)	Hold Time (Min)	Power Limit (%)
1	150	30	10	3	90
2	210	30	5	10	90
3	50	30	1	20	0

Table 1: Titan MPS digestion method.

Calibration Standards

External calibration was used for the analysis. A 1000 mg/L Cl aqueous stock solution was used for the preparation of the working standards and quality control (QC) solution. The concentrations in each standard were 6, 12, 24, 48 mg/L.

Instrumentation and Method Parameters

The measurements were performed using PerkinElmer's Avio 220 Max ICP-OES using the instrument conditions in Table 2. Axial viewing and a MEINHARD® nebulizer were chosen for higher sensitivity. The RF power was set to 1500 watts, the plasma gas to 8 L/min and the nebulizer gas to 0.55 L/min, allowing all analyses to be completed with a total argon consumption of 9 L/min, a direct result of the unique Flat Plate plasma technology.

Parameter	Value
Plasma View Mode	Axial
Nebulizer	MEINHARD®
Spray Chamber	Baffled Glass Cyclonic
Torch	1- slot Quartz
Injector	2.0 mm ID Alumina
RF Power	1500 W
Plasma Gas Flow	8 L/min
Auxiliary Gas Flow	0.2 L/min
Nebulizer Gas Flow	0.55 L/min
Integration Time	1-5 sec
Read Delay	20 s
Replicates	3
Sample Uptake Flow	1.5 mL/min

Table 2: Avio 220 Max ICP-OES instrumental conditions.

Results and Discussion

The wide wavelength range of the Avio 220 Max ICP-OES enables the unique ability to measure wavelengths above 800 nm. In this analysis, Cl 858.579 nm was used for Cl determination. The calibration plot is shown in Figure 1. The excellent linearity (correlation coefficients > 0.9999) demonstrates the ability to accurately and consistently measure Cl 858.579 nm.

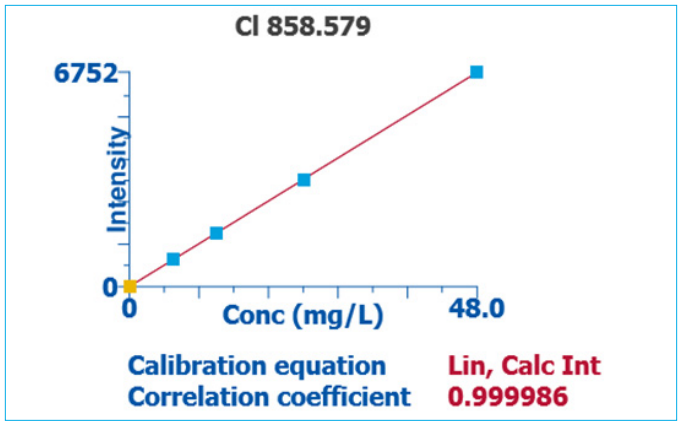

Figure 1: Calibration plot for Cl.

The sample results are shown in Table 3. The content of Cl in the palm tree ranged from 0.23-0.69% between the different parts of the palm tree, with the highest levels found in the palm trunk and leaf. Taking the dilution factor into consideration, the results also show that the Avio 220 Max ICP-OES has sufficient detection capability for chlorine determination below 10 ppm in solution.

Palm Tree Component	Cl (% in Solid)
Palm leaf	0.68
Fruit brunch	0.48
Trunk	0.69
Fronds	0.23

Table 3: Chlorine content in various parts of the palm tree.

Since the sources of chlorine are primarily from water, fertilizers, pesticides, and soil, 3-MCPD in the palm oil can be avoided by minimizing the use of chlorine-containing substances during cultivation.

Figure 2 compares the results between the Avio 220 Max ICP-OES and titration methods, showing that the two methods produce very similar results, with differences less than 10%.

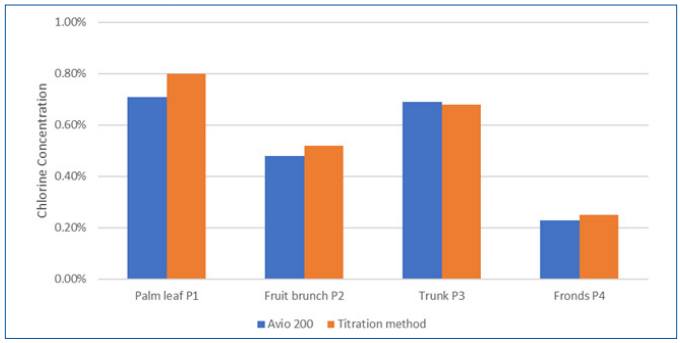

Figure 2: Comparison of results measured using the Avio 220 Max ICP-OES and the titration method.

In addition, the accuracy of the method was validated by analyzing a quality control (QC) standard, spiked at the midpoint of the calibration curve. As shown in Table 4, a recovery of 96% was obtained, well within acceptable limits.

Sample	Spiked Conc. ppm	Measured Conc. ppm	Recovery %
QC 24 ppm	24	23.1	96.3

Table 4: Cl recovery in a QC standard.

Conclusion

This work demonstrated the unique advantage of the Avio 220 Max hybrid simultaneous ICP-OES for the accurate measurement of chlorine in palm trees. In comparison with the traditional titration method which can only measure one element of Cl, the Avio 220 Max ICP-OES provides a fast, simple and reliable method for simultaneous determination of Cl, while offering the multi-element capability to measure other elements in palm trees, as well as throughout the refining process, in one analysis. Combined with smart Syngistix™ for ICP software features to enhance user experience, the multi-elemental capability of the Avio 220 Max provides a signficant return on investment, especially when compared to dedicated chlorine analyzers.

References

1. MPOB Statement on 3-MCPD Esters https://pdf4pro.com/view/mpob-statement-on-3-mcpd-esters-36dba3.html.
2. Catrina Ng, *"Early Detection of Chloride in 3-MCPD Precursors in Palm Oil Through the Analysis of Chloride in Edible Oil with the Avio 2220 Max ICP-OES"*, PerkinElmer Application Note, 2021.

Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black (0.76 mm id), PVC	09908587
Drain Tubing, Red/Red (1.14mm id), PVC	09908585
50 mL Autosampler Tubes, Qty 500	B0193234

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