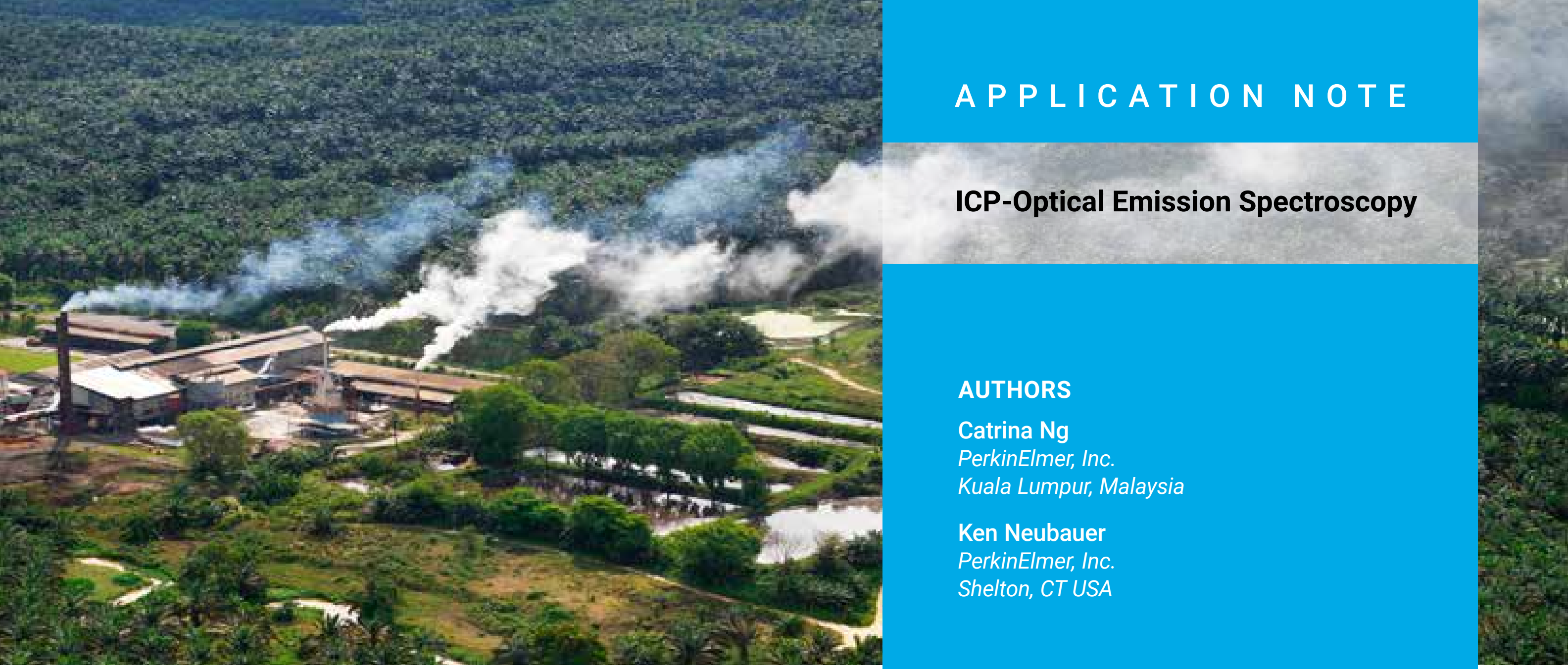

APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Analysis of Midstream Refining Products from Palm Oil Processing with the Avio 220 Max Hybrid Simultaneous ICP-OES

Introduction

Palm oil and its byproducts are used in a wide variety of industries and products, including foods, pharmaceuticals, personal care, energy, agriculture, as well as in the production of oleochemicals. With such wide and varied uses, palm oil production is continuously increasing, with Malaysia and Indonesia being the world's largest producers. In both countries, there are numerous large palm plantations and associated milling, refining, and processing facilities.

Extracting and refining oil from palm trees and fruits is a complex, multi-step process which can be generalized into three categories: upstream, midstream, and downstream processes. Upstream processes involve milling the palm (known as the fresh fruit bunch) and extracting the crude palm oil (CPO), as well as monitoring the environment where the trees are grown (i.e. soil, water, and fertilizer). The CPO represents the natural levels of elements in the palm. Much of this monitoring can be done by ICP-OES using the Avio® Max family of instruments.[1-4]

After milling, the CPO goes to the refinery, where it is turned into purified products through a number of steps, including degumming, bleaching, deodorizing, and separating the refined oil into its separate components, as shown in Figure 1. This is referred to as midstream processing.

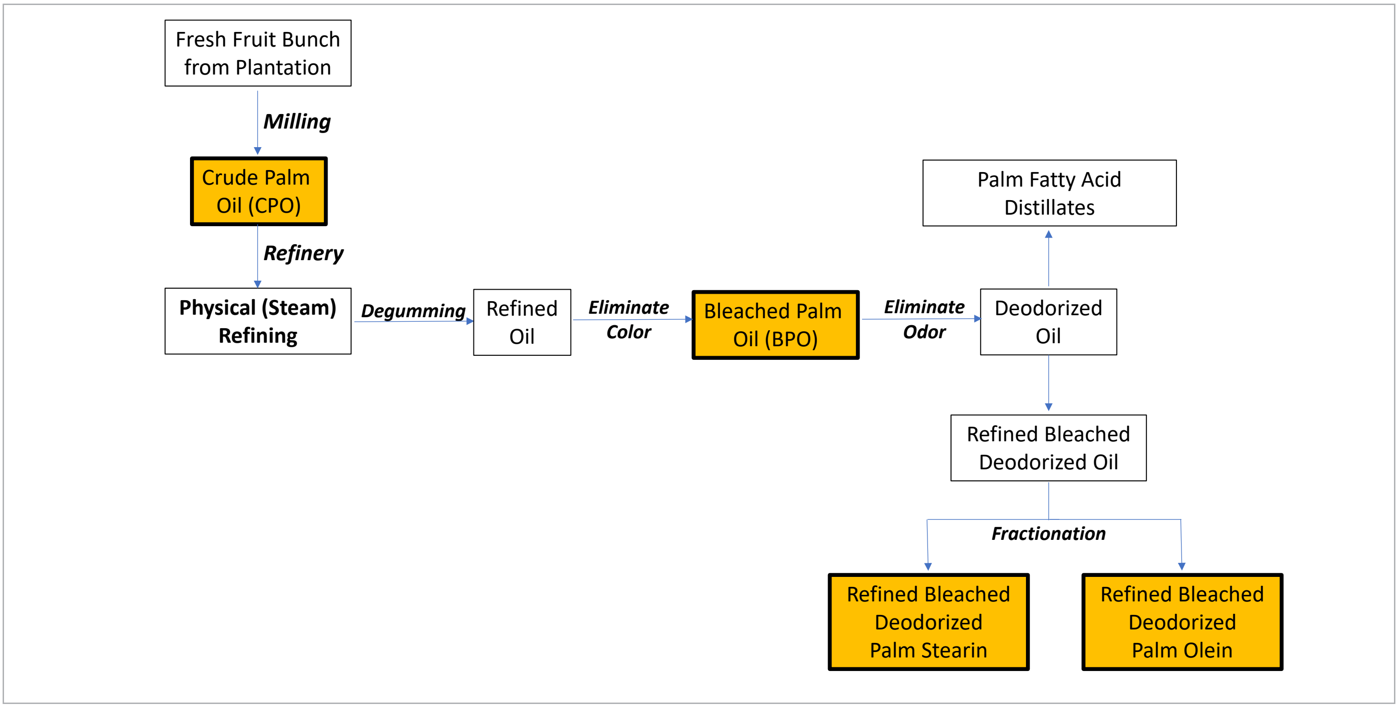

Figure 1. Midstream refining process of crude palm oil. Products in orange were studied in this work.

Downstream processes focus on converting the midstream processes into final products for consumer and industrial use.

During the midstream refining process, the CPO, intermediates, and final products must be monitored for quality. Critical elements which must be monitored are phosphorus (P), iron (Fe), copper (Cu), and nickel (Ni) which are oxidizing agents that turn the oil rancid. Therefore, the concentration of these elements must be controlled; knowing these concentrations in the CPO is crucial for determining the refining parameters required to remove them. In addition, the mineral content (calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na)) must also be monitored for product labelling.

This work focuses on the analysis of critical elements in the midstream refining processes of palm oil using the Avio 220 Max hybrid simultaneous ICP-OES, a unique ICP-OES solution ideally suited to the palm oil industry.

Experimental

Samples and Sample Preparation

Five different samples were obtained from the midstream process of a palm oil refinery: crude palm oil (CPO), bleached palm oil (BPO), refined bleached deodorized palm stearin (RBDPS) and two samples of refined bleached deodorized palm olein (RBDPL) taken from different batches. These products are shown in the orange boxes in Figure 1. Samples were prepared by adding a known quantity of sample to PTFE vessels and bringing them to a final weight with V-Solv™, for a final dilution of 10x (i.e. 3 g of sample brought to a final weight of 30 g with V-Solv™). The V-Solv™ was spiked with 6 ppm cobalt (Co), which was used as an internal standard. In this way, the internal standard was added to all samples, blanks, and calibration standards through sample dilution. Any spikes were added to the samples before the addition of V-Solv™. The samples were then heated at 65 °C until they dissolved, then maintained at 65 °C during the analysis.

PTFE vessels were chosen since polypropylene vessels leach phosphorus with V-Solv™. Glass vessels were also evaluated, but they had significant contamination for calcium, magnesium, potassium, and sodium at the concentration levels of interest.

Calibration standards were prepared by weight from organometallic stock solutions, as shown in the Consumables Used table at the end of the document. In addition, 75 cSt mineral oil was added to all standards and blanks to closely matrix-match the prepared samples. The standards and blanks were brought to a final weight using V-Solv™ (which contained Co) at the nominal concentrations shown in Table 1. All quantitative measurements were made against external calibration curves.

Table 1. Calibration Standards.

Element	Standard 1 (µg/kg)	Standard 2 (µg/kg)	Standard 3 (µg/kg)
Ca, Cu, Fe, Mg, Ni	10	20	40
P	100	200	400
Na, K	250	500	1000

Instrumental Conditions

All analyses were performed on the Avio 220 Max hybrid simultaneous ICP-OES using the conditions in Table 2. The wavelengths and plasma viewing heights are listed in Table 3. Because these palm oil refining products only remain soluble in V-Solv™ at 65 °C, a heated spray chamber (PC^{3X}, Elemental Scientific Inc., Omaha, Nebraska, USA) was used and maintained at 65 °C throughout all analyses.

The Avio Max family of ICP-OES instruments employs Flat Plate™ plasma technology, a unique innovation which provides several advantages compared to plasmas produced with conventional load coils[5], including high matrix tolerance and the ability to decompose sample matrices, especially solvents.

When running organic solvents, the high carbon load must be dealt with, both to prevent carbon deposition and minimize spectral interferences. Physically, a higher-than-normal auxiliary gas flow was used to adjust the base of the plasma about 2 mm above the tip of the injector to prevent carbon deposition on the injector. The Avio 220 Max system uses PlasmaShear™ technology, another proprietary feature which physically cuts off the top of the plasma (as shown in Figure 2) to prevent carbon deposition on the interface window, eliminating the need for interface cones and their associated maintenance. Systems without PlasmaShear require the addition of oxygen to prevent carbon deposition and attain long-term stability when aspirating solvents. While oxygen addition works well, it increases the complexity of the system, as a mass flow controller must be added to control and optimize the oxygen flow. Furthermore, the addition of oxygen decreases analyte intensity, which is especially important when analyzing sulfur, an important element in biodiesel produced from palm oil.

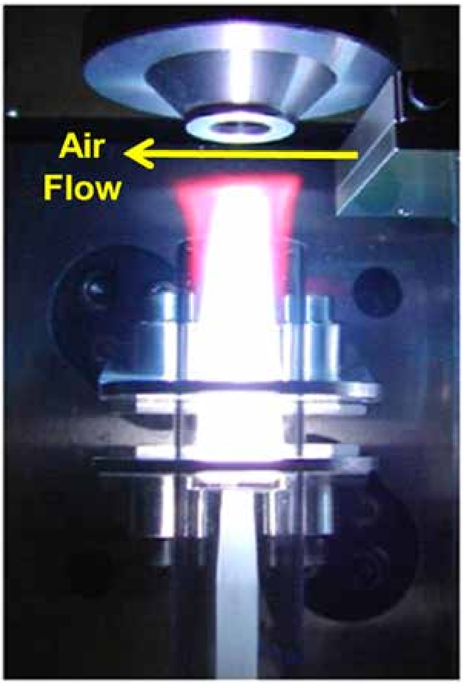

Figure 2. PlasmaShear technology cutting off the top of the plasma.

Spectrally, the effects of carbon were minimized in several ways. First, carbon loading in the plasma was reduced by using a low-flow GemCone™ nebulizer, a 1.2 mm injector, and a sample uptake rate of 0.8 mL/min. Carbon background was minimized by making all measurements in radial plasma view. Although these strategies limit carbon-loading of the plasma, they also decrease the intensity of the analyte signal. However, due to its unique optical design, the Avio 220 Max has outstanding sensitivity, which still allows accurate, reproducible measurements of low concentration analytes. In addition, the most sensitive wavelengths were selected for analytes. Because Na and K are atom lines and have low ionization potentials (Na = 5.1 eV, K = 4.3 eV), the viewing height in the plasma was optimized to give the best signal-to-background ratios in a carbon matrix.

The auto integration capability was used to find the best compromise between accuracy and analysis time, as the Avio 220 Max determines the optimum integration time and number of readings based on the analyte intensities acquired during a pre-shot. Once the data was acquired, peak integration was simplified by using auto background correction.

Table 2. Avio 220 Max ICP-OES Instrumental Parameters and Conditions.

Parameter	Value
Sample Uptake Rate	0.8 mL/min
Nebulizer	Low-flow GemCone
Spray Chamber	PC^{3x}, 65 °C
RF Power	1500 W
Torch	3-slot Avio torch for organics
Injector	1.2 mm ceramic
Plasma Flow	10 L/min
Aux Gas Flow	1.1 L/min
Nebulizer Gas Flow	0.45 L/min
Torch Position	-3
Replicates	3
Auto Integration Range	0.5 - 5 sec
Plasma View	Radial

Table 3. Analytes and Wavelengths.

Element	Wavelength (nm)	Plasma Viewing Height (mm)
P	213.620	15
Ni	221.650	15
Fe	259.942	15
Mg	280.271	15
Cu	324.752	15
Ca	393.366	15
Na	589.592	9
K	766.490	13
Co (Internal Standard)	228.616	15

Results and Discussion

The analyte concentrations in the samples appear in Figure 3. Although neither Ni nor Na were detected in any of the samples, the effect of the refining process is clearly evident: the CPO contains the highest concentrations of all analytes (except Cu), with the finished products (RBDPS, RBDPL) generally containing the lowest concentrations. The differences in concentrations between RBDPL-1 and RBDPL-2 reflect the differences between the batches. The refining process removes the elements which promote oxidation (P, Fe, Cu), with concentrations decreasing by up to two orders of magnitude. Likewise, the mineral concentrations decrease by up to three orders of magnitude through refining.

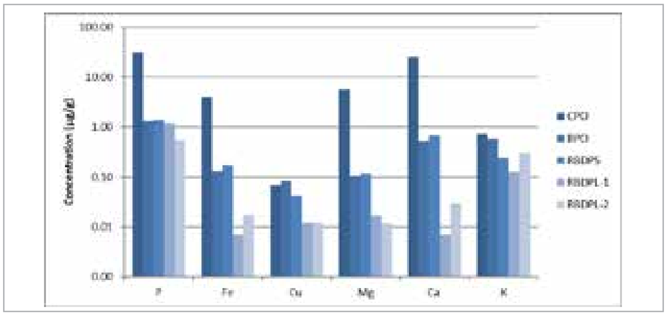

Figure 3. Results for five samples during the refining process of palm oil. (Ni was not detected in any of the samples.)

For the elements which promote oxidation, each refinery sets its own limits for different stages of the refining process. By using the "Limits" function in Syngistix™ for ICP software, samples which are above (or below) user-defined limits are instantly visible in Data Viewer, as shown in Figure 4 for the midstream palm oil processing samples. In these samples, phosphorus is above the user-defined limits for all samples except for RBDPL-2, while Fe is only above the limits for the CPO and is removed through the processing to be below the limit. Both Ni and Cu are below the limits for all samples, indicating that they are not a concern for causing rancidity, while Mg, Ca, Na, and K are monitored but do not have limits which must be met during the refining process.

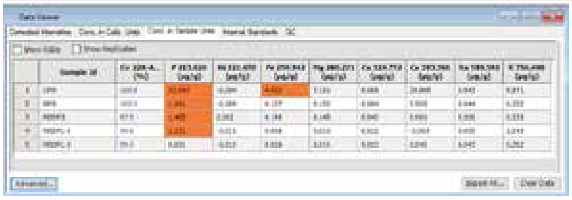

Figure 4. Syngistix software's Data Viewer automatically highlighting samples which are above user-defined thresholds.

Since certified reference materials are not available for these samples, accuracy was evaluated through spike recovery studies, where one of the RBDPL samples was spiked at concentrations equivalent to the middle calibration standard. As shown in Figure 5, each spike sample was analyzed three times, with all analytes in all samples recovering within 10% of their true values, demonstrating the accuracy of the methodology.

With the accuracy established, the stability was evaluated by measuring a sample of CPO 16 times. Since CPO is the least refined sample, it also has the most complex matrix, making it the most challenging sample to analyze. The internal standard recovery is plotted in real time during an analytical run in Data Viewer, as shown in Figure 6 during 16 analyses of CPO. With variations of less than 5% and an RSD of 1.0% across the 16 samples, the stability of the methodology is established.

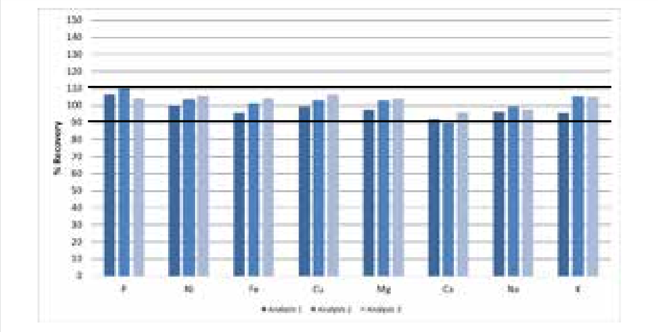

Figure 5. Recoveries in RBPDL spiked at the levels of Calibration Standard 2.

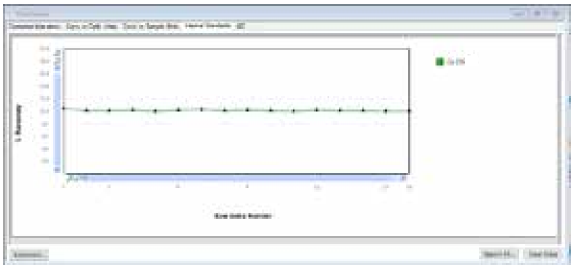

Figure 6. Stability of internal standard (Co) during 16 consecutive analyses of CPO, as displayed in Syngistix software's Data Viewer.

After assessing the internal standard stability in CPO, the stability of the analytes was assessed from the same run. As shown in Figure 7, the analyte signals varied by less than ±10% (concentrations normalized to the first sample) with RSDs of less than 3.0% across the 16 measurements. Neither Ni nor Na were detected in the CPO.

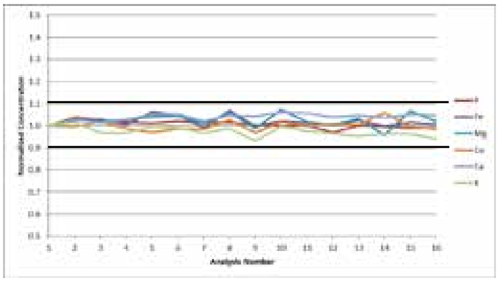

Figure 7. Analyte stability in 16 consecutive analyses of CPO.

To assess the stability of Ni and Na, spikes of all analytes were added to BPO at the concentration of Calibration Standard 2, and the spiked sample measured 16 times. As shown in Figure 8, the stability is equivalent to CPO, with variations of less than ±10% for all analytes across the 16 samples.

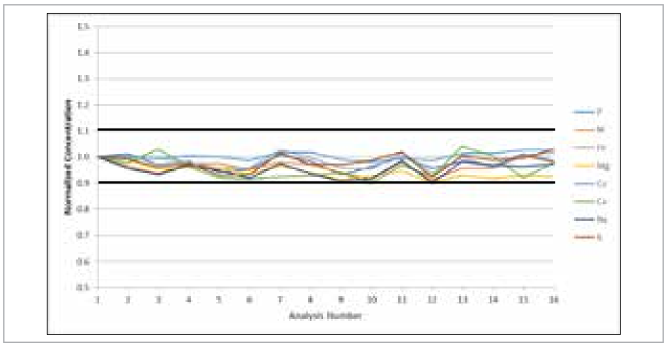

Figure 8. 16 analyses of BPO spiked with all analytes at Calibration Standard 2 concentrations.

Finally, detection limits were determined with the Detection Limits feature in Syngistix software, where the standard deviation of 10 measurements of the calibration blank (i.e. V-Solv™ + mineral oil) was multiplied by 3. Figure 9 shows the determined detection limits in solution; multiplying these values by 10 (to account for sample preparation) would give detection limits of the samples. The detection limits in the samples are well below the limits for the elements which promote rancidity of the palm oil.

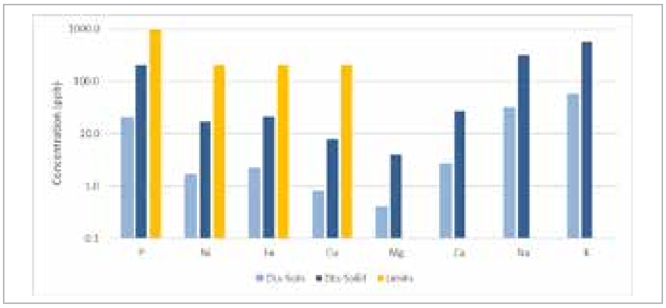

Figure 9. Detection limits in solution (light blue) and sample (dark blue), along with limits (orange).

Conclusions

This work has demonstrated the ability of the Avio 220 Max hybrid simultaneous ICP-OES to successfully measure important analytes in a variety of midstream products from the palm oil refining process. With its unique optical design and outstanding sensitivity, effects of carbon can be minimized, while still allowing low levels to be accurately and repeatedly measured. The incorporation of PlasmaShear technology prevents deposition of carbon on the interface, resulting in low maintenance requirements. The combination of high sensitivity and low maintenance makes the Avio 220 Max an ideal tool for the palm oil industry to monitor intermediates and products in upstream, midstream, and downstream processing.

Consumables Used

Component	Part Number
Low-Flow GemCone Nebulizer	N0770358
PC^{3x} Temperature-controlled Spray Chamber	N0790959
1.2 mm i.d. Alumina Injector	N0791182
Hybrid XLT 3-Slot Torch	N0790249
Black/Black (0.76 mm i.d.) Solvent Flex Peristaltic Pump Tubing for Sample Uptake	00473550
Red/Red (1.14 mm i.d.) Solvent Flex Peristaltic Pump Tubing for Drain	09923037
PTFE Digestion Tubes, 55 mL	N9308024
V-Solv™ Solvent	N9308265 (1 gallon) N9308378 (5 gallons)
Hydrocarbon Oil, 75 cSt	N0776103 (500 mL) N9308262 (1 gallon)
V23 Wear Metals Standard, 100 µg/g	N9308245 (100 g) N0776105 (200 g) N9308318 (400 g)
Phosphorus Standard in Hydrocarbon Oil, 1000 µg/g	N9308221
Potassium Standard in Hydrocarbon Oil, 1000 µg/g	N9308222
Sodium Standard in Hydrocarbon Oil, 1000 µg/g	N9308227
Cobalt Internal Standard, 6% in Mineral Spirits	N0776107 (200 g) N9308334 (400 g)

References

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