FIRST Newsletter

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Rapid Quantification of P, S, Cl, and Ca in Vegetable Oils – Without Sample Preparation

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Nowadays, vegetable oils are not only used in the kitchen for cooking, frying, and baking. They are also used in large quantities to produce foodstuffs, in the pharmaceutical and cosmetics industries, and to manufacture many other industrial products. Some, especially high-quality edible oils can be produced gently by cold pressing and subsequent filtration, but most oils are processed by refining in several industrial process steps. Typical process steps during refining are degumming, neutralization, and bleaching. In these process steps, special attention is paid to monitoring the phosphorus concentration, since particularly in the degumming step, interfering phospholipids are removed, as these have a negative effect on subsequent process steps as well as on the properties of the refined oil.

Depending on the involved production processes and the final application of the vegetable oils, monitoring other elements is also of interest. Sulfur, for instance, needs to be kept below certain thresholds, often <10 ppm when refining used cooking oils (UCO) into biodiesel. Moreover, the chlorine concentration needs to be determined to prevent possible formation of harmful Cl compounds at higher refining process temperatures, such as 3-monochloro-1,2-propanediol (3-MCPD) esters. And calcium is of interest as it can be used to optimize the refining process.

Fig. 1: Compact EDXRF S2 POLAR for fast and easy onsite process control.

Today these elements are often determined by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). Due to the high operational efforts, requiring educated laboratory personnel and time-consuming sample preparation, ICP-OES instruments are

rarely used at refinery plants and are simply not suitable for 24/7 process control. So why not choose polarizing Energy Dispersive X-Ray Fluorescence (EDXRF) technique for such an analytical task? Polarized EDXRF measurements can not only be performed much easier and faster when using the S2 POLAR, the technique also allows to reduce the operational costs substantially.

Instrumentation

The S2 POLAR EDXRF spectrometer is the ideal solution for your vegetable oil analysis. The combination of closely coupled beam path with its polarized excitation enables optimal sample excitation, resulting in outstanding analytical performance. In comparison to ICP-OES, which requires daily re-calibration, a simple one-time calibration makes the S2 POLAR ready for your application! Once the system is calibrated, the TouchControl™ user interface makes it easy to run routine samples directly after a short introduction.

Bruker's unique SampleCare™ technology (Fig. 2) protects all vital system components in the event of liquid cup leakage. Hence, SampleCare is key for high system uptime and short and easy maintenance, especially when analyzing vegetable oils.

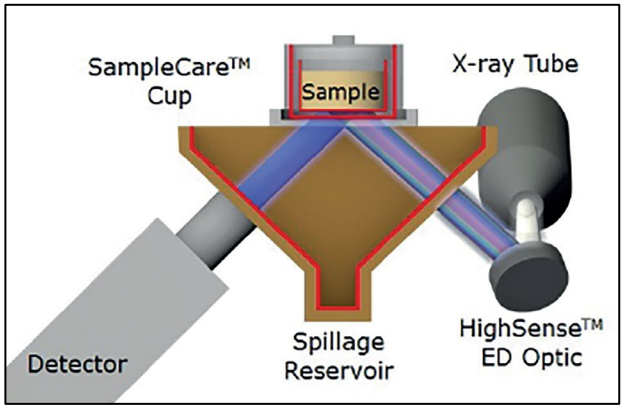

Fig. 2: S2 POLAR SampleCare™ technology with HighSense™ beam path.

Sample Preparation

Perfect samples for XRF measurements are clear, homogenous solutions which do not contain any particles or immiscible phases. Such samples, typically refined oils and clear process samples can be easily measured with excellent reproducibility and in perfect agreement with ICP-OES results. On the other hand, unrefined process samples of vegetable oils or used cooking oil samples often contain particles, some suspension or turbidity (Fig. 3).

Fig. 3: Unrefined, crude palm oil samples.

For this report, to minimize the impact of such in-homogeneities, the standard operation procedures have been further optimized by using smaller sample amounts, shorter measurement times as well as some heat-treatment immediately before the measurement. Samples have been measured in a standard liquid cup equipped with Prolene film with a thickness of 4 µm.

Calibration

Sets of matrix-matched vegetable oil standards have been used to calibrate the S2 POLAR. Typical used calibration ranges for P are up to 2000 ppm P (Fig. 4), up to 1000 ppm for S, up to 100 ppm for Cl (Fig. 5), and up to 1000 ppm for Ca. The sets also contain blank samples, suitable quality control (QC) samples for lower

and higher concentration ranges as well as drift control (DC) samples ensuring long-term stability of the calibration. Such matrix-matched standards are available on request for the S2 POLAR and can be used for factory calibrations.

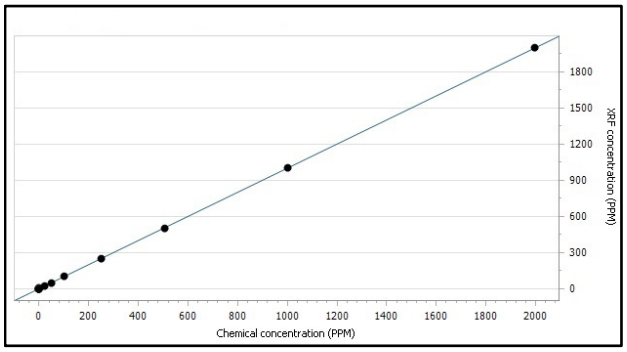

Fig. 4: Calibration curve for P calibration in vegetable oil for the concentration range of 0 to 2000 ppm P.

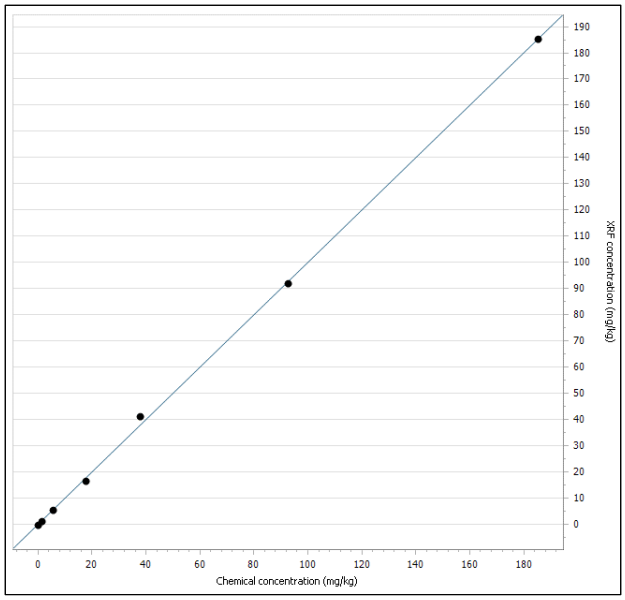

Fig. 5: Calibration curve for Cl in vegetable oil for the lower concentration range of 0 to 50 ppm Cl.

Results

Various types of vegetable oils such as sunflower, rapeseed, soja, and palm oil have been analyzed as well as samples collected at different intermediate process steps. The following figures and tables highlight some of the results. Figures 6 and 7 show overlaid Cl signals and overlaid P signals, respectively, of crude palm oil samples at a low concentration range, with an excellent separation of neighboring elements lines.

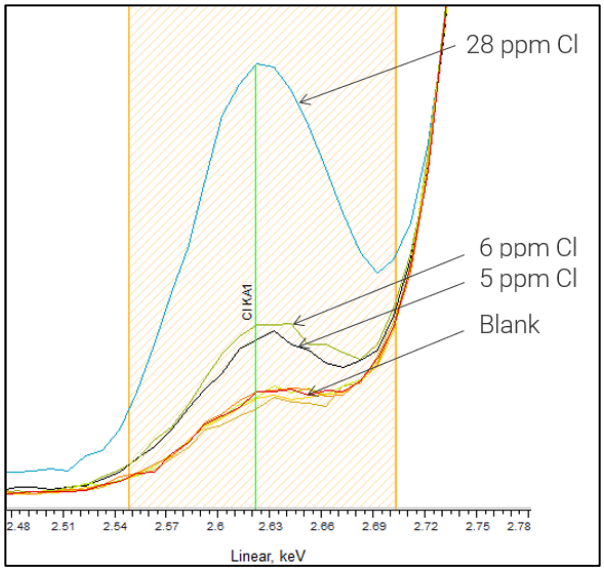

Fig. 6: Overlaid Cl signals of crude palm oil samples, the yellow shadowed area is integrated for measurements.

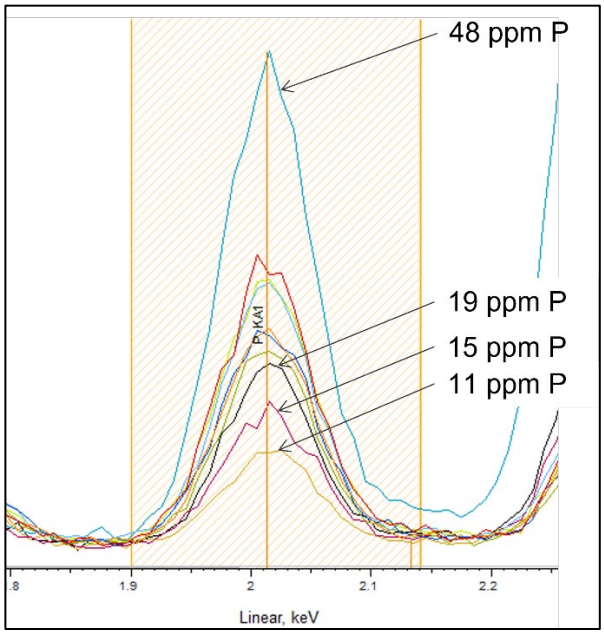

Fig. 7: Overlaid P signals of crude palm oil samples, the yellow shadowed area is integrated for measurements.

Table 1 shows the analytical repeatability of P in crude palm oil. By using the S2 POLAR, the results are available within minutes after sampling. In contrast, the AOCS (American Oil Chemists' Society) reference method requires hours of sample preparation.

Table 2 shows the results of another repeat-ability test, analyzing P in a rapeseed oil sample before degumming. The measurements reveal a slightly higher variability due to the different properties of unrefined rapeseed oils – still, the advantage of polarized EDXRF is clear: Much shorter time-to-result!

Table 1: Repeatability test of P in Crude Palm Oil (CPO).

Measurement #	P [ppm]
CPO #1	22.3
CPO #2	22.8
CPO #3	22.0
CPO #4	22.6
CPO #5	22.6
CPO #6	22.4
CPO #7	21.8
CPO #8	22.8
CPO #9	22.5
CPO #10	21.7
Average	**22.33**
Std. Dev.	**0.35**
Rel. Std. Dev.	**1.58%**
Ref. Value (AOCS)*	**22.2**

* Reference value determined by AOCS (American Oil Chemists' Society) method

Table 2: Repeatability test of P in rapeseed oil before degumming.

Measurement #	P [ppm]
Rep #1	470
Rep #2	499
Rep #3	500
Rep #4	450
Rep #5	455
Average	**475**
Std. Dev.	**21.2**
Rel. Std. Dev.	**4.5%**
ICP-OES Ref. Value	**460**

Figure 8 shows an overlay of 10 measurements of a rapeseed oil sample containing 5.0 ppm P. Although the concentration level of P is quite low, the overlaid signals of the sample (blue colors) show excellent repeatability.

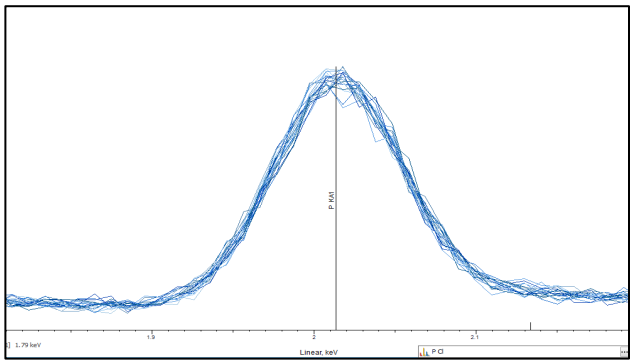

Fig. 8: Overlay of 10 measurements of a rapeseed oil sample with a P concentration of 5.0 ppm.

Conclusion

Polarized EDXRF is the ideal analytical tool for fast and reliable monitoring of various elements in vegetable oils. Beneficial is the simple sample preparation ensuring a short time-to-result and lower costs of ownership in comparison to conventional ICP-OES technique. The multi-element capability of the S2 POLAR allows accurate monitoring of key elements relevant for the oil refinery process control and final product evaluation. Bruker's unique SampleCare technology protects vital system components and is essential for high system uptime required by industrial sites.

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