application note

The Analysis of Phosphorus in Edible Oils by ICP-OES

Introduction

Inductively coupled plasma optical emission spectrometry (ICP-OES) provides a rapid and highly sensitive method for the determination of total phosphorus in commercial food oils. Total phosphorus provides a measure of phospholoid content, higher levels of which are known to be a key parameter in premature darkening of the oil
with heating, as well as increases unfavourable flavours [(1)].

Commonly an application performed by graphite furnace atomic absorption (GFAA), the lower sensitivity provided by this technique combined with complications associated with the most appropriate choice of matrix modifier, encouraged researchers to find a simpler alternative technique. Complications in modifier selection were primarily due to the presence of multiple gaseous forms of phosphorus that are thermally stable over a wide temperature range.

With the advent of significantly lower priced ICP-OES instruments bridging the price gap between it and GFAA, ICP-OES has proved to be the ideal technique that both researchers and cost conscious laboratories have been looking for. *Sample preparation is greatly simplified* with the elimination of the requirement for a modifier to ensure accurate and precise determinations of the highly temperature dependent phosphorus. *Method development is significantly reduced* through the elimination for the need to search for the optimum combination of heating and matrix modification to achieve suitable results[(2)].

Along with these labour saving improvements, ICP-OES also provides other cost savings which include *faster sample analysis times*, typically less than one minute to measure phosphorus in an oil sample compared to approximately 5 minutes per sample for GFAA.

Other time and cost saving advantages offered by ICP-OES includes the reduction of the number of solutions required to be prepared and analysed per sample, since ICP-OES avoids the need to prepare standard addition solutions (essential in GFAA to address the inconsistencies between commercial food oils). This need for further sample dilutions is also eliminated by ICP-OES due to the wide linear concentration range available.

Finally, the phosphorus in edible oils application is one example where ICP-OES offers a sensitivity advantage over GFAA, with ICP-OES achieving at least *a threefold improvement in the P detection limit*.

This paper describes the parameters and conditions required for the determination of phosphorus in edible oils. However, note that the described parameters can also be used for the determination of the many other elements required to be measured in edible oil allowing you to take advantage of the multielement capabilities offered by ICP-OES.

Experimental

Integra Operating Parameters

As Integra provides computer control of over 200 instrument parameters, operating parameters optimized for the individual elements can readily be determined and stored in method files to be recalled at any time for analysis. Integra's unique and sophisticated auto-optimisation software can be used to optimize the operating parameters according to user specified optimization criteria driven by the application. In this application, the instrument was optimized for maximum performance on P.

The optimized set of parameters were:

Viewing Height	
Individually Optimised	6 mm
Power	1300 w
*** Nebuliser Flow**	
Optimised for P	0.45 L/min (170 kPa)
Plasma Gas Flow	12 L/min
Auxiliary Gas Flow	1.0 L/min
Total Gas Flow	13.4 L/min

Sample Uptake Rate	8 rpm 1.0 mL/min)
PMT Voltage	600 V
Measurement Conditions for Detection Limit	
Integration Time	10 s
Replicates	11
Background Correction	Fixed Point
Scan Windows	0.027 nm 3rd Order 0.02 nm 4th Order
Data Points	50
Integration Time/Data Point	0.2 s
Measurement Conditions for Sample Analysis	
Integration Time	2 s
Replicates	3
Background Correction	Dynamic
Scan Windows	0.027 nm 3rd Order 0.02 nm 4th Order
Data Points	50
Integration Time/Data Point	0.2 s

* The optimum nebuliser flow can change for different nebulisers so should be checked (and optimised) at time of method development.

Standard & Sample Preparation

Edible oil samples are prepared by a 1 in 5 dilution achieved gravimetrically by accurately weighing 10 g of sample and diluting to 50 g with kerosene. Ensure the sample is thoroughly mixed. This dilution ratio ensures that both standards and samples have similar viscosity, which is not possible if the edible oil is not diluted. Whilst dilution ratios as low as 1 to 1 are also possible (where analyte sensitivity may be an issue), there is a risk that samples and standards may not be matrix matched. If the levels of the analytes in the edible oil are sufficiently low to require a 1 in 1 dilution, then standard additions or spike recovery is the preferred mode of calibration and analysis.

Standard preparation is achieved by using Conostan[3] organometallic standards. These are prepared from alkylarylsulphonates in a base oil and are available as individual concentrates or multi-element blends. Conostan standards are extremely stable and easy to handle and are soluble in ketones, paraffinic and aromatic hydrocarbons. A 1 ppm P standard was prepared gravimetrically by accurately weighing 0.5 g of 100 ppm Conostan S-21 multi element organometallic standard and making up to 50 g with kerosene.

Results And Discussion

Typical Detection Limits

The detection limit reported is based on 3 standard deviations of the blank using 11 replicates of 10 s integrations.

Wavelength	GFAA	Integra
ICP-OES		
P 213.618 nm	0.15 mg/kg	0.025 mg/kg (5 ppb in solution)
P 177.495 nm	Not Detected	0.04 mg/kg (8 ppb in solution)

Typical Reproducibility with High Resolution ICP-OES

A common interference encountered in the analysis of P by ICP-OES is the interference caused by Cu at the most sensitive P 213.618 nm wavelength. Under normal circumstances, this type of spectral interference in ICP-OES would be overcome by selecting an alternative interference free wavelength (P 177.495 nm). Whilst this may result in a compromise in sensitivity through the selection of a less sensitive but interference free wavelength, the compromise in sensitivity in this example is marginal (0.04 mg/kg compared to 0.025 mg/kg). However, the P 177.495 nm wavelength also suffers from interference by Cu. Choosing the third most sensitive P wavelength at 178.284 nm results in an order of magnitude drop in P sensitivity.

This dilemma is easily overcome with the use of 1800 g/mm holographic grating option on the Integra ICP-OES. This high resolution grating option offers high intensity spectra at P 213.618 nm when used in higher orders resulting in the complete resolution of the Cu on P interferences, allowing the selection of the most sensitive P wavelength required for the application.

Figure 1a shows the Cu on P interference using an ICP-OES offering 0.009 nm resolution. Figure 1b shows the same example, this time on the Integra ICP-OES 1800 g/mm holographic grating. Used in third order, the 0.007 nm resolution clearly resolves the Cu on P interference to the baseline.

The impact of Integra's high resolution grating on the accuracy of analysis of P in edible oils is seen in Table 1. This table shows the concentration of soybean oil containing 0.1 ppm of P in the presence of Cu

measured using high resolution and normal resolution modes.

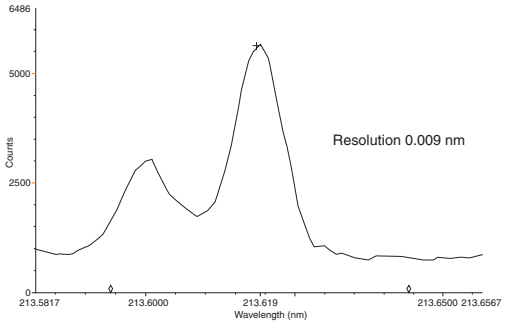

Figure 1a. 1 ppm Cu Interference on 1 ppm P at the 213.618 nm wavelength.

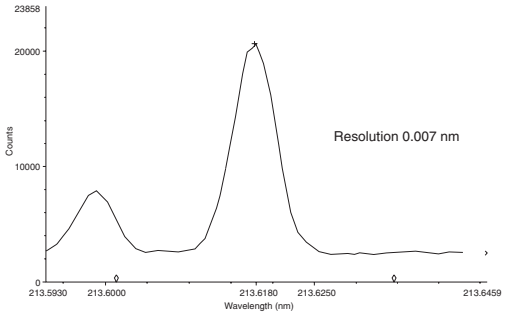

Figure 1b. 1 ppm Cu completely resolved from 1 ppm P at the 213.618 nm wavelength.

	Normal Resolution (0.009 nm)	High Resolution (0.007 nm)
P 213.618	0.17 ppm	0.10 ppm
P 177.495	0.14 ppm	0.10 ppm

Table 1. Accuracy and Reproducibility of Integra's High Resolution ICP-OES when measuring 0.1 ppm P in the presence of Cu.

The 0.009 nm resolution results in poor accuracy with significant over-recoveries caused by Cu interference and also poor reproducibility with the two P wavelengths generating two totally different P results. Clearly, Integra's high 0.007 nm resolution ensures high accuracy and reproducibility with both primary and secondary P wavelengths achieving 100% recoveries, even in the presence of Cu.

Conclusion

The Integra ICP-OES greatly simplifies the P in edible oils application. It has become the technique of choice for cost conscious laboratories working towards reducing costs and at the same time, improving productivity in today's highly competitive environment.

For laboratories currently considering GFAA for P in edible oils, cost saving benefits of the Integra ICP-OES include:

1. Simplified sample preparation through:
   - the elimination of the requirement for a modifier
   - the reduction in the number of samples and standards to be prepared. Since ICP-OES does not require standard additions, the number of samples to be prepared is reduced by a factor of 4 (assuming 4 point standard addition curves)
   - the reduction in sample dilutions required due to the wider linear dynamic range

2. The reduction in method development time because the need to search for the optimum combination of heating and matrix modification to achieve suitable results is eliminated

3. Productivity enhancements through:
   - faster sample analysis times of less than 1 minute per sample compared to 5 minutes for GFAA
   - reduction in the number of solutions to be analysed with a factor of 4 improvement in productivity achieved simply by the elimination of the requirement for standard additions.

In addition to the above cost saving advantages, the Integra high resolution ICP-OES offers at least a three fold improvement in sensitivity ensuring the highest possible accuracy and reproducibility in the analysis of P in edible oils.
For laboratories currently considering ICP-OES for P in edible oils, benefits of the Integra ICP-OES include:

- High resolution optics that ensure complete freedom from interferences in the analysis of P in edible oils.
- High sensitivity for all elements ensuring both high accuracy and reproducibility of analysis.
- Computer Control of All Operating Parameters which allows fully automated instrument optimisation and setup so that even first time ICP-OES users can maximise the performance and productivity of their ICP.
- Mass flow control of the most critical parameter, the gas flow through the nebuliser, which allows the highest possible analytical precision, as well as immediate diagnosis of nebuliser blockages commonly encountered for this application.

- Low cost operation with the economies of a low argon flow torch (typically less than 13 L/min) and low power plasma (typically 1300 w).

References

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GBC Scientific Equipment Pty Ltd
A.C.N. 005 472 686

12 Monterey Road, Dandenong, Victoria, 3175, Australia
Phone: +61 3 9213 3666 Fax: +61 3 9213 3677
E-mail: gbc@gbcsci.com URL: www.gbcsci.com