Direct Analysis of Ca, P, and Fe in Oleochemicals by Inductively Coupled Plasma MS

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ABSTRACT: This paper presents the use of inductively coupled plasma MS (ICP-MS) for direct elemental analysis in oleochemicals (long-chain fatty acid derivative). It focuses on Ca, P, and Fe, which are key elements for many industrial applications and which are known to be challenging for MS technology. The instrument is operated with a "shield torch" interface under "high-power cool plasma." In addition, oxygen is blended with argon to prevent buildup of carbon on both torch and cones. The extra sensitivity of the ICP-MS technology permits high dilution factors, thereby minimizing any potential matrix effects. The contents of Ca, P, and Fe are quantified by standard addition. There is no need to resort to interference corrections for P, because it is measured as its oxide PO^+. Detection limits lie in the sub-ppm for Ca and P and in the low-ppb for Fe. Accuracy of the method has been demonstrated for our products by a recovery test.

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KEY WORDS: Direct ICP-MS analysis of organics, oleochemicals, quantification of Ca, P, and Fe.

The chemical industries require the routine trace analysis of elements, both to meet the requirements of speciality chemical markets and to monitor specific processes. The analytical tools must be able to quantify various elements from ppm to ppb in a wide range of matrices to meet the demand of food (1,2), personal-care (3), pharmaceutical (4), or electronic applications (5). In addition, control of manufacturing (6) is often limited by the rapidity of the overall analytical process. Thus, sample preparation for routine work must remain simple and quick.

Despite its high purchasing cost, inductively coupled plasma-mass spectrometry (ICP-MS) (7–9) has become the method of choice for fast trace-level elemental analysis in aqueous solutions (10). However, until recently, extension of this technique to the direct quantification of elements in organic matrices has been hindered by technical issues (11–13). Its use in routine analysis is restricted to the determination in organic solvents of impurities present in the ppb range (14); these are rather simple organic products that generate a limited number of spectral interferences. When dealing with products characterized by more complex matrices, most publications still resort to extensive sample pretreatment (15–18), which is time-consuming and may lead to erroneous results due to contamination or loss of volatile elements. In a few cases only, microemulsification (including water in oil) has been reported as an alternative way of introducing organic samples (19).

This paper investigates the use of ICP-MS technology for direct trace elemental analysis of oleochemicals after a simple dilution operation. These products are characterized by complex matrices, often containing relatively high levels (up to 100 ppm) of alkali and alkaline-earth metals as impurities. This study focuses on Ca, P, and Fe, which are key for many speciality chemicals and which are known to be challenging for the MS technology. They all suffer (20) from either isobaric interferences (especially ^{40}Ar on ^{40}Ca, and also ^{54}Cr on ^{54}Fe) or polyatomic interferences (e.g., $^{12}C^{16}O_2$ on ^{44}Ca; $^{40}Ar^{16}O$ on ^{56}Fe; $^{36}Ar^{18}O$ on ^{54}Fe; $^{40}Ar^{16}O^{1}H$ on ^{57}Fe; $^{14}N^{16}O^{1}H$, $^{15}N^{16}O$, and $^{12}C^{18}O^{1}H$ on ^{31}P). The poor ionization of phosphorus in the plasma (7) (about 33%) further complicates its determination. Therefore, this element is measured as PO^+ (mass 47), because it readily forms oxides (21), and the potential interferences (from, e.g., Ti, Zr^{2+}, Mo^{2+}, ArLi) that could hamper the quantification are not expected in our standard samples. This method of measurement avoids both the need for interference corrections (12) that are not always reliable and the use of a high-resolution ICP-MS or dynamic reaction cell (21) that requires heavy investment. It is therefore suitable for routine operation.

The application has benefitted from the latest technical developments: The ICP-MS instrument is equipped with a "shield torch" interface, that is, a grounded metal plate to shield the plasma from the RF (radio frequency) coil. In addition, the plasma power is set to 950 W; the combination of relatively high plasma power with long sampling depth and high carrier gas flow rates generates a "high-power cool plasma." These conditions minimize the background spectroscopic interference by avoiding reionization of polyatomic clusters, without reducing the sample matrix decomposition. Oxygen is blended in the argon to prevent buildup of carbon on both torch and cones. To avoid plasma overloading, the diluted samples are introduced by direct aspiration using a micronebulizer (22) and a cooled spray chamber (13).

Furthermore, a simple and pragmatic method has been adopted to facilitate routine analysis. *N*-Methyl pyrrolidone (NMP) has been selected as it solubilizes all our oleochemical products; in addition, water can be used as co-solvent, reducing somewhat the NMP aggressiveness (all negative effects of the very strong solvent properties of this product), the negative effects of the organic solvent on the plasma, and the sensitivity to frequent small variations of water content characterizing our

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samples. NMP also allows quantification using aqueous standards, which are more economical and easier to handle than oil standards. Since the routine samples generally contain Ca and P at ppm levels and Fe in the sub-ppm range, their determination does not require the very low detection capability of the MS. The extra sensitivity of the instrument enables us to further dilute the samples, thereby minimizing any potential matrix effects. Quantification of the three elements of interest is carried out by standard addition.

This method has been validated for a typical oleochemical product [i.e., long-chain fatty acid (FA) derivative]. Calibration curves, intermediate precision (as measured by the reproducibility over a one-month period), quantification limit, and recovery are reported. Certified reference materials made of an oleochemical matrix and the elements of interest are not available to further evaluate the accuracy of the proposed methodology.

EXPERIMENTAL PROCEDURES

Instrumental setup. We used the ICPMS 7500a of Agilent (Palo Alto, CA) with the "shield torch" system and both platinum sampling and skimmer cones. The instrument was fitted to a quartz T-connector (AHF analysentechnik) and a quartz torch (1.5 mm i.d., Agilent), both specifically designed for organic solvents. The sample introduction system included a Glass Expansion MicroMist nebulizer (50 μL), a Glass Expansion Easy-Fit sample tube (0.25 mm i.d., 1.6 mm o.d.), and a quartz spray chamber with a polyetrafluoroethylene endcap (Agilent).

Preparation of samples and standards. The oleochemical samples (long-chain FA derivatives) to be analyzed have a dynamic viscosity of up to 9000 mPa·s (25°C). To minimize any matrix effects, these organic products are dissolved (dilution factor of 55) in a solution of NMP (VLSI grade from J.T.Baker) containing 10% deionized water (18 M ohm) and 0.5% ultrapure nitric acid (Ultrex II grade from J.T.Baker). The same solution of NMP, H_2O, and HNO_3 is used as a blank, since we cannot obtain oleochemical products totally free of element.

To keep the analytical procedure simple, standard addition is carried out using two stock solutions, the first one containing 1 ppm Fe and the second one containing 10 ppm of Ca and P. Both stock solutions are prepared by dilution with a 5% nitric acid solution of the relevant 1000 ppm single-element water standards [respectively, Fe_2O_3, $Ca(NO_3)_2$, and $NH_4H_2PO_4$ standards; from CPI International). The spike levels for each element are selected to cover typical concentration ranges: 5, 10, 25, and 50 ppb for Fe; and 50, 100, 200, and 300 ppb for Ca and P (as PO). The diluted and spiked samples are introduced into the plasma by self-aspiration.

The recovery test has been carried out by spiking a known amount of the three single-element metallo-organic oil standards (from CPI International, 1000 ppm) to a typical oleochemical sample matrix.

Analytical conditions. Table 1 shows typical operating conditions characterizing the "high-power cool plasma" mode presented in the Introduction section. These parameters have been selected based on the ^{59}Co response (single isotope with a mass close to the elements of interest), using a blank solution NMP/H_2O/HNO_3 spiked with 10 ppb of Co (from Merck). The operating conditions are then carefully adjusted to get the optimal response for ^{40}Ca and ^{47}PO, using solutions of Ca (10 ppb) and PO (10 ppb). The number of counts per time unit recorded for the selected ion is compared with those characterizing the background (mainly C_2^+ and ArC^+), while slowly increasing the parameters of interest. Besides the torch parameters, the sensitivity is greatly affected by the flows of carrier, makeup, and optional gas.

TABLE 1
ICP-MS Parameters Under "High-Power Cool Plasma" Mode for Direct Elemental Analysis of Oleochemicals in NMP/H_2O/HNO_3[a]

Parameter	Setting	Parameter	Setting
RF power	950 W	Carrier gas	0.78 L/min
RF matching	1.70 V	Makeup gas	0.42 L/min
Sampling depth	14.0 mm	Optional gas	8.5%
Torch—H	−0.4 mm	S/C temperature	−2°C
Torch—V	−0.6 mm		

[a] ICP, inductively coupled plasma; NMP, *N*-methyl pyrrolidone; RF, radiofrequency; S/C, spray chamber.

The selected operating conditions result in low maintenance requirements: Sampling and skimmer cones have shown neither clogging nor deterioration. They have been thoroughly inspected on a regular basis using a microscope and have required cleaning less than once every two months. Both torch and torch-interface are replaced by a second set weekly, and the spray chamber and nebulizer are cleaned every two weeks.

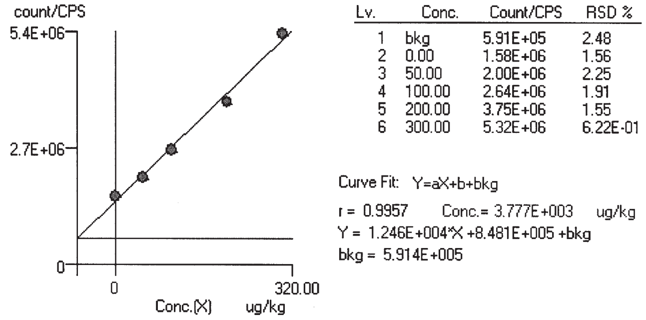
Statistics. Basic calculations were performed using Microsoft Excel 2000; repeatability and reproducibility were calculated by a "Mixed procedure" in SAS® System for Windows (SAS, Gary, NC).

RESULTS AND DISCUSSION

Quantification of Ca, P, and Fe by standard addition. Figures 1, 2, and 3 show the calibration curves calculated after standard addition in a typical sample for, respectively, Ca (isotope 40), P [measured as PO (mass 47)], and Fe (isotope 56). The concentrations found after extrapolation have been corrected by the dilution factor of 55 to get the content in the test sample of the three elements of interest.

Detailed investigation of these calibration curves gives a good overview of the quantification method. After correction for the background level by blank subtraction, the plots for PO and Fe are characterized by good linearity ($r > 0.999$). As expected, the oxidation process leads to a smoother slope for PO. Determination of P level does not seem to be limited by the offset, since the background level at mass 47 is very stable. Quantification of Fe in the test sample suffers somewhat from the too-high spike concentration. The levels have been selected based on maximum specification requirements.

For Ca, the correlation coefficient is somewhat lower ($r > 0.995$), and there is a significant offset due to remaining Ar spectral interferences. As we do not have a real blank, the background correction is approximate. In addition, all points of the



Lv.	Conc.	Count/CPS	RSD %
1	bkg	5.91E+05	2.48
2	0.00	1.58E+06	1.56
3	50.00	2.00E+06	2.25
4	100.00	2.64E+06	1.91
5	200.00	3.75E+06	1.55
6	300.00	5.32E+06	6.22E-01

Curve Fit: Y=aX+b+bkg

r = 0.9957 Conc.= 3.777E+003 ug/kg

Y = 1.246E+004*X +8.481E+005 +bkg

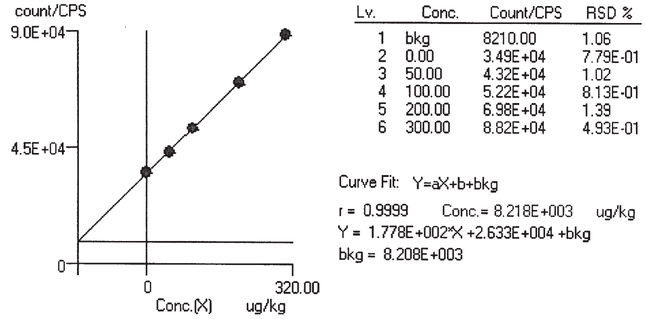
bkg = 5.914E+005

FIG. 1. Calibration curve calculated after standard addition and direct inductively coupled plasma-MS (ICP-MS) analysis for the quantification of ^{40}Ca in a typical sample [long-chain fatty acid (FA) derivative].

corresponding line have been recorded by the "analog mode" of the detector, with the exception of the background. Thus, it is likely that quantification of this element by standard addition suffers from the high background level of the blank and from the fact that the background cannot be accurately corrected.

The above results could not be confirmed by looking at alternative isotopes: No correlation at ^{44}Ca, ^{54}Fe, ^{57}Fe, or ^{31}P could be found ($r < 0.5$), and hence their limit of quantification could not be determined. This is expected because, as already described in the Introduction section, they all suffer from interactions involving argon, nitrogen, carbon, and oxygen. These latter elements are present in the plasma at high levels, and their concentration is difficult to control as they are issued from the surrounding atmosphere or from the matrix. Each would require a very specific optimization for their quantification. Therefore, the accuracy of our results needs to be checked by another procedure—in our case the recovery method.

Intermediate precision. The intermediate precision of the total method (including sample preparation) has been measured by analyzing the same test sample in triplicate and repeating this operation four times within a one-month period. The average values (AVG) and the SD calculated for the reproducibility data are summarized in Table 2 for the three elements of interest. For reference, the SD corresponding to the within-run repeatability are also shown.



Lv.	Conc.	Count/CPS	RSD %
1	bkg	8210.00	1.06
2	0.00	3.49E+04	7.79E-01
3	50.00	4.32E+04	1.02
4	100.00	5.22E+04	8.13E-01
5	200.00	6.98E+04	1.39
6	300.00	8.82E+04	4.93E-01

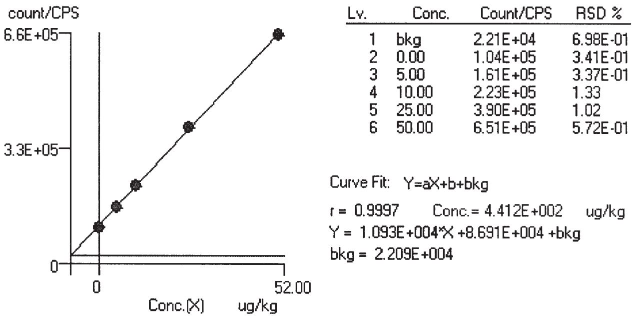
Curve Fit: Y=aX+b+bkg

r = 0.9999 Conc.= 8.218E+003 ug/kg

Y = 1.778E+002*X +2.633E+004 +bkg

bkg = 8.208E+003

FIG. 2. Calibration curve calculated after standard addition and direct ICP-MS analysis for the quantification of ^{47}PO in a typical sample (long-chain FA derivative). For abbreviations see Figure 1.



Lv.	Conc.	Count/CPS	RSD %
1	bkg	2.21E+04	6.98E-01
2	0.00	1.04E+05	3.41E-01
3	5.00	1.61E+05	3.37E-01
4	10.00	2.23E+05	1.33
5	25.00	3.90E+05	1.02
6	50.00	6.51E+05	5.72E-01

Curve Fit: Y=aX+b+bkg

r = 0.9997 Conc.= 4.412E+002 ug/kg

Y = 1.093E+004*X +8.691E+004 +bkg

bkg = 2.209E+004

FIG. 3. Calibration curve calculated after standard addition and direct ICP-MS analysis for the quantification of ^{56}Fe in a typical sample (long-chain FA derivative). For abbreviations see Figure 1.

The intermediate precisions measured for the Ca and P relative SD (RSD) of, respectively, 11 and 5% are limited by the repeatability, as expected from the characteristics of the corresponding calibration curves described in the previous paragraph. Results for Fe (RSD ~18%) would be improved by reducing the spike addition to better match the unexpectedly low level of the element in the sample.

Accuracy. Because certified reference products comprising a similar oleochemical matrix and the elements of interest are not available, the accuracy of the method for our products has been evaluated by a recovery test. The spike levels are given in Table 2, together with the results of the experiment. The recovery values vary between 92 and 103%, indicating an adequate accuracy. This conclusion has been confirmed by comparison of our results with ICP-atomic emission spectrometry measurements.

Limit of quantification. In theory, the limit of quantification (LOQ) for each analyte is given by the following formula (23):

$$\text{LOQ} = 10 \times \sigma_{\text{blank}} \frac{c_s}{X_s} \quad [1]$$

where σ_{blank} is the SD of the blank signal; c_s is the concentration of the standard; and X_s is the average signal for the standard in the sample matrix.

However, an oleochemical sample free of all three analytes is not available and the use of blank (NMP/water/HNO_3) would give an unrealistically low SD. Therefore, a high-side estimate of the quantification limit has been calculated by assuming the following: σ_{blank} is the SD corresponding to the within-run repeatability for a typical sample; c_s is the amount of analyte in the metallo-organic oil standard; and X_s is the average signal for this oil standard in the sample matrix.

As expected from the calibration curves (Figs. 1–3), only the quantification limit calculated for Fe falls in the ppb range. With the present method, quantification of both Ca and P is limited to the low ppm range. These results confirm the adequacy of the method for our samples. In the case of nonroutine applications requiring lower detection limits, the ICP-MS sensitivity could still be used by analyzing an aqueous solution after pretreatment of the samples.

TABLE 2
Calculation of Reproducibility, Repeatability, and Recovery of the Direct ICP-MS Analysis (including sample preparation) for a Typical Sample[a] (long-chain FA derivative)

	Sample before spike				Sample after spike		
		SD				SD	
	AVG	Within run	Between runs	Spike	AVG	Within run	Between runs
Ca	3.8	0.41	0.41	1.03	4.9	0.77	0.77
P	8.2	0.38	0.38	4.01	11.7	0.36	0.37
Fe	0.39	0.03	0.07	0.49	0.81	0.05	0.12

[a] All data reported as ppm.

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