



## Analytical Methods

# Multielemental analysis in vegetable edible oils by inductively coupled plasma mass spectrometry after solubilisation with tetramethylammonium hydroxide



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## ABSTRACT

Trace metals have negative effects on the oxidative stability of edible oils and they are important because of possibility for oils characterisation. A single-step procedure for trace elemental analysis of edible oils is presented. To this aim, a solubilisation with tetramethylammonium hydroxide (TMAH) was assayed prior to inductively coupled plasma mass spectrometry detection. Small amounts of TMAH were used, resulting in high elemental concentrations. This method was applied to edible oils commercially available in Argentina. Elements present in small amounts (Cu, Ge, Mn, Mo, Ni, Sb, Sr, Ti, and V) were determined in olive, corn, almond and sunflower oils. The limits of detection were between  $0.004 \mu\text{g g}^{-1}$  for Mn and Sr, and  $0.32 \mu\text{g g}^{-1}$  for Sb. Principal components analysis was used to correlate the content of trace metals with the type of oils. The two first principal components retained 91.6% of the variability of the system. This is a relatively simple and safe procedure, and could be an attractive alternative for quality control, traceability and routine analysis of edible oils.

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## 1. Introduction

Quantification of trace element in edible oils is an important criterion for their quality regarding their freshness, storability and toxicity (Kabata-Pendias, 2010; R. Castillo, S. Jimenez, & Ebdon, 1999). Some trace elements can increase the rate of oil oxidation, whilst others are very important to monitor due to their toxicity and metabolic role. The contents of some trace elements are legislated in different types of edible oils. For instance, the International Olive Council (IOC) has established as a quality criterion a maximum residue level (MRL) for the content of As, Cu, Fe, and Pb in olive oils and olive-pomace oils and the maximum levels of Cu and Fe in other vegetable oils have been also legislated, varying from  $0.1$  up to  $5.0 \mu\text{g L}^{-1}$  (IOC, 2011).

The content of metals in edible oils depends on several factors. They might come from the soil, environment, genotype of the plant, fertilizers and/or metal-containing pesticides, introduced during the production process (by processing actions, such as bleaching, hardening, refining and deodorization) or by contamination from the metal processing equipment (Giacomo et al., 2004;

Kabata-Pendias, 2010; Kelly, Heaton, & Hoogewerff, 2005; R. Castillo et al., 1999).

The industry requires fast, precise and cheap analytical methods for the determination of these elements. However, the quantification of metals in organic samples has always been a challenge in analytical chemistry, focusing mainly on samples such as oils, petroleum products, pharmaceutical or industrial organic samples and food products (Llorent-Martínez, Ortega-Barrales, Fernández-de Córdova, Domínguez-Vidal, & Ruiz-Medina, 2011). Sample preparation is one of the most relevant and critical step in the whole analytical procedure. Conventional sample preparation methods for spectrometric techniques involve solubilisation of the organic matrix requiring extensive pre-treatment before their analysis, such as digestion at elevated temperatures with mineral acids with oxidizing properties, or hydrogen peroxide (Benincasa, Lewis, Perri, Sindona, & Tagarelli, 2007). However, these steps are capable of causing sample contamination. Besides, the high temperature frequently reached during the procedures can cause losses of the most volatile elements (Anderson, 2008).

As an alternative approach for organic sample preparation the use of a strong alkaline reagent such as tetramethylammonium hydroxide (TMAH) has been proposed (Martins, Pozebon, Dressler, & Kemieciki, 2002; Matusiewicz & Golik, 2004; Nóbrega et al., 2006). A methanolic solution of TMAH could be used properly for

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several biological samples previously to trace element analysis with spectrometric techniques (da Silva, Borges, da Veiga, Curtius, & Welz, 2003; Giacomelli et al., 2002; Pozebon, L. Dressler, & J. Curtius, 1998, 2000; Ribeiro, Curtius, & Pozebon, 2000; Ribeiro, Moretto, Arruda, & Cadore, 2003; Silva, Santelli, Willie, Sturgeon, & Sella, 1999; Yan Zhou, Keong Wong, Lin Koh, & Chin Wee, 1996). In addition, TMAH could work as a solubiliser of fatty tissues and it has been applied for human hair sample preparation, as well as for aquatic plants, lobster hepatopancreas, dogfish muscle and liver solubilisation (Almeida & Lima, 2000; Darke & Tyson, 1994; Ebdon, Foulkes, & Sutton, 1997; Gregoire, Miller-Ihli, & Sturgeon, 1994; Martins et al., 2002; Pozebon et al., 2000; Ribeiro et al., 2000; Silva et al., 1999; Tsalev, Slaveykova, & Georgieva, 1996; Tsalev, Slaveykova, & Mandjukov, 1990; Vanhaecke, Boonen, Moens, & Dams, 1995; Willie, Conrad Gregoire, & Sturgeon, 1997). To the best of our knowledge, there is not available evidence of using TMAH regarding to the determination of trace elements in oils.

The inorganic mass spectrometry with inductively plasma (ICPMS) outstands among the available analytical techniques. Usually, the introduction of digested and diluted samples is required to limit the amount of dissolved solids and organic matter. Since samples can influence the overall performance causing several problems related to instability or even extinction of the plasma (Chaves, de Loos-Vollebregt, Curtius, & Vanhaecke, 2011; Santelli, Oliveira, de Carvalho, Bezerra, & Freire, 2008). Another negative effect over injector, cones and lens blockage, is the carbon deposits from incomplete oxidation of the organic matrix. Moreover, severe spectral and non-spectral interferences could occur with complex matrices. In ICPMS, these drawbacks have been overcome by the addition of oxygen into the plasma to aid oxidation of the organic matter or by decreasing the temperature using a cooled spray chamber (dos Santos et al., 2007; Edlund, Visser, & Heitland, 2002); thus carbon deposition on the torch can be minimised or even avoided, while a number of interferences are mitigated (Kahen, Jorabchi, Gray, & Montaser, 2004).

The purpose of the present work was to investigate and optimise the experimental conditions for ICPMS on the determination of trace elements in oil samples dissolved with TMAH. The studied parameters included sample preparation conditions (heating, amount of TMAH, etc.), and instrumental operating conditions (sample intake flow rate, oxygen-auxiliary gas, spray chamber desolvation temperature, ICP radio frequency power). Once optimised, the proposed method was applied to the determination of Cu, Ge, Mn, Mo, Ni, Sb, Sr, Ti, and V in olive, corn, almond and sunflower oils from Argentina. The proposed method was also compared with the conventional microwave acid digestion. Moreover, principal components analysis (PCA) was used to correlate the content of trace metals with the type of oils.

## 2. Materials and methods

### 2.1. Instrumentation

An inductively coupled plasma mass spectrometer, Perkin-Elmer SCIEX, ELAN DRC-e (Thornhill, Canada) was used. The argon gas with a minimum purity of 99.996% was supplied by Praxair (Córdoba, Argentina). An HF-resistant and high performance perfluoracetate (PFA) nebulizer model PFA-ST, coupled to a quartz cyclonic spray chamber with internal baffle and drain lines, cooled with the PC<sup>3</sup> system from ESI (Omaha, NE, USA) was used.

Tygon black/black 0.76 mm i.d. and 40 cm length peristaltic pump tubing was used. The instrument conditions were: auto lens mode on, peak hopping measurement mode, dwell time of 15 ms, 30 sweeps per reading, 1 reading per replicate and 3 replicates.

Nickel sampler and skimmer cones were used. For comparison purpose, the samples were also digested in a microwave digestion system model START-D from Milestone (Soriso, Italy), and Milestone hermetically sealed 100 mL internal volume, 1-cm wall thickness polytetrafluoroethylene (PTFE) reactors, using a two steps programme (10 min up to 200 °C and up to 1000 W and kept by 15 min at 200 °C, up to 1000 W). The digested samples were analysed by ICPMS using cross-flow nebulizer and Scott-type spray chamber and external calibration with Rh as internal standard. A water bath HH-S water bath from Arcano (Argentina) was also used for sample pre-treatment digestion.

### 2.2. Reagents and samples

Ultrapure water (18.2 MΩ) was obtained by an Easy pure RF system from Barnstead (Dubuque, IA, USA). Concentrated nitric acid (65%v/v) from Sigma-Aldrich (Germany), methanol from Fisher-Scientific (Lawn, NJ, USA), hydrogen peroxide (40%v/v) from Parafarm (Argentina), tetramethylammonium hydroxide pentahydrate from Sigma-Aldrich (USA), Dimethylformamide from Acroorganics (New Jersey, USA), formic acid (98/100%v/v) from Fisher Scientific (UK), were used throughout. Multi-element standard solution 2, 3 and 5 (10 mg L<sup>-1</sup>) from Perkin Elmer Pure Plus Atomic Spectroscopy Standard, (Norwalk, USA), Rh mono-elemental standard solution (10 mg L<sup>-1</sup>) from Perkin Elmer Pure Plus, Atomic Spectroscopy Standard, (Norwalk, USA), and a setup/mascal solution from Perkin Elmer Pure Plus, Atomic Spectroscopy Standard, (Norwalk, USA), were used. The analysed samples were commercially available oils from Argentina: three different almond oils, six different sunflower oils, three different corn oils and, five different species of olive oils, were analysed.

### 2.3. Analytical procedure

In order to select adequate sample digestion and optimise ICPMS conditions, olive oil samples were selected to carry out experiments. Oils were accurately weighed (0.5 g) in 50 mL metal-free polypropylene flasks. Then, increasing amounts (0.0, 2.5, 5.0, 10.0, 15.0, and 20.0 %v/v) of TMAH were added. The mixtures were vigorously shaken and kept at 90 °C in a water bath during 30 min. After that, flasks were diluted up to 50 mL mark with 1% nitric acid solution. Oil samples were spiked with multi-element standard solutions to final concentrations of 40 µg L<sup>-1</sup>, and were used to optimise nebulizer and oxygen gas flow rates, sample flow rate, and radio frequency (RF) power of ICPMS. A blank solution was always measured and taken into consideration. The starting conditions were: 500 µL min<sup>-1</sup> sample flow rate; 1000 W RF power and 0.9 L min<sup>-1</sup> nebulizer gas flow rate before their optimization.

For comparative purposes, acid treatments assisted by microwaves were carried out. To this aim, 0.5 g of oil were mixed with 7 mL of HNO<sub>3</sub> and 1 mL of H<sub>2</sub>O<sub>2</sub> in PTFE flasks and then was submitted temperature programme (10 min ramp to 180 °C and 20 min step at 180 °C). Finally, samples and reagent blanks were diluted to 50 mL with ultrapure water.

For the external calibration against aqueous standards, all solutions were prepared in 1% nitric acid. For the matrix matching calibration in organic medium, the solutions were prepared in 15 %v/v TMAH and 1% nitric acid. Analytes concentrations in both calibrations were 10, 20, 40, 80, and 100 µg L<sup>-1</sup>. Standards, samples and blanks were added with Rh (40 µg L<sup>-1</sup>) as internal standard.

### 2.4. Data analysis

PCA is an unsupervised technique and allows relationships between variables and observations to be identified and structure in the data to be detected. PCA reduces the dimensionality of the

original data matrix by constructing PCs that are linear combinations of the original variables (Helena et al., 2000). Only those PCs with eigenvalues greater than unity were retained. Infostat 2012 software was used for statistical calculations (Di Rienzo et al., 2011).

### 3. Results and discussion

#### 3.1. Instrument optimization

Small amounts of organic compounds in the plasma can raise the nebulization and aerosol transport efficiencies, increasing the signal compared to aqueous solutions. Moreover, organic compounds can also improve the ionisation efficiency of high ionisation energy elements by carbon charge transfer reactions (Boorn & Browner, 1982; dos Santos et al., 2007; Hu, Hu, Gao, Liu, & Lin, 2004; Tormen, Chaves, Saint-Pierre, Frescura, & Curtius, 2008). However, carbon derived from solvents and oils, could condense on the cones and lens, generating plasma instability, resulting in loss of detection power. As a consequence of the improper ionisation conditions, it was mandatory an overall instrument performance optimization.

For the actual analyses, sample introduction was accomplished using the combination of a microconcentric nebulizer and a baffled cyclonic spray chamber at room temperature (22 °C), and cooled to 3 and –5 °C. The optimization was performed with a solution of olive oil sample treated as discussed above (Section 2.3). The argon gas flow rate (nebulizer) (ArFR) and RF power were optimised for maximum analyte intensity.

##### 3.1.1. Argon flow rate

The nebulizer gas flow rate was optimised to be applied to all elements. Fig. 1(a) showed that most analytes signals increased with ArFR up to 0.7 and 0.8 L min<sup>-1</sup>. Additionally, the behaviour of selected carbon-containing polyatomic ions was evaluated in terms of this parameter in order to establish the operational conditions with the lowest background contribution due to sample matrix. The results showed in Fig. 1(b) suggested that 0.75 L min<sup>-1</sup> was the best condition due to high analyte intensity signal and low background due to carbon input. This situation improved when the desolvation temperature was –5 °C.

##### 3.1.2. ICP radiofrequency power

The radiofrequency power was systematically optimised aiming to obtain the best signal to background ratio for each analyte. The

optimum recorded radiofrequency powers versus ionisation energy of the analytes were compared for Cu, Ge, Mn, Mo, Ni, Sb, Sr, Ti, and V. The condition selected were: temperature of spray cooled chamber –5 °C, analyte concentration 10 µg L<sup>-1</sup> for all the analytes, sample FR: 500 µL min<sup>-1</sup> and ArFR: 0.75 L min<sup>-1</sup>. The RF powers recorded were between 950 and 1100 W and the ionisation energies were between 5.7 and 8.8 eV. Thus, a 1000 W radiofrequency power was chosen as compromise condition. Regarding to carbon-based polyatomic ions, it could be pointed out that the higher the RF power, the higher the polyatomic ion formation due to carbon.

##### 3.1.3. Sample flow rate

The sample flow rate (SFR) is directly related to the nebulizer efficiency enabling direct control of the sample input to the ICP and consequently the amount of carbon. It could be noted that when increasing SFR, the signal for all analytes remained almost constant at the three temperatures evaluated, evidencing the high performance of the PFA nebulizer. The sample flow rate of 500 µL min<sup>-1</sup> was thus established as compromise for all further experiments. Regarding to the recorded background, the contribution of the polyatomic ions <sup>13</sup>C<sup>18</sup>O<sup>16</sup>O<sup>+</sup> and <sup>1</sup>H<sup>12</sup>C<sup>16</sup>O<sup>+</sup> was negligible under the optimized conditions (discussed above).

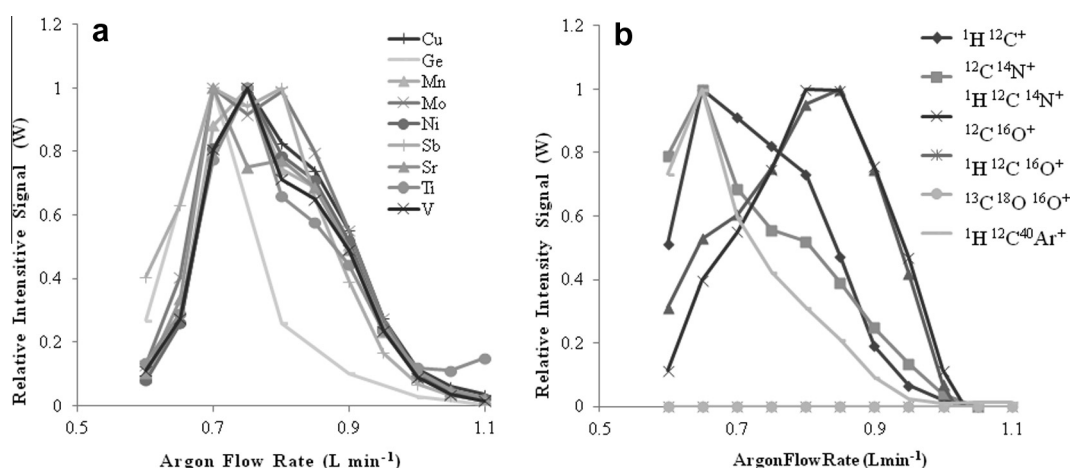
##### 3.1.4. Adding O<sub>2</sub> as auxiliary carrier gas

Oxygen gas as auxiliary carrier gas has been employed with success to reduce the contribution of carbon-based polyatomic ions to the background and to avoid depositions and blockage of cones and lenses (dos Santos et al., 2007; Woods & Fryer, 2007). Accordingly, a sample solution containing the analytes was prepared following the recommended procedure (Section 2.3) and the relative analyte signals were contrasted in terms of the oxygen gas flow rate. A blank solution containing only the reagents was also assayed.

The outcomes indicated that all analytes showed maximum signals between 0.02 and 0.06 mL min<sup>-1</sup>. A sole exception was observed in the case of Ge with a maximum at 0.1 mL min<sup>-1</sup>. Overall, an O<sub>2</sub> flow rate of 0.04 mL min<sup>-1</sup> was established as optimum for the entire research.

#### 3.2. Analytical performance

Table 1 displays the figures of merit for the trace elements determination in edible oil samples treated with TMAH, and



**Fig. 1.** (a) Effect of Ar flow rate on the relative intensity signal of the analytes, for sample solution treated as proposed. (b) Effect of Ar flow rate on polyatomic ions formation for an aqueous solution containing 15 %v/v TMAH solution. Analyte concentration: 10 µg L<sup>-1</sup> for all the analytes. The signal intensity was related to the higher value obtained for each curve. (Sample flow rate: 500 µL min<sup>-1</sup>, RF power of 1000 W, temperature of spray cooled chamber –5 °C).

**Table 1**  
Figures of merit for the trace elements determination in edible oil samples treated with TMAH using a microconcentric nebulizer as introduction sample system (proposed method) or after sample digestion using a conventional nebulizer (conventional method).

Analyte	Isotope (a.m.u.)	Proposed method (TMAH treatment)			Conventional method (MW treatment)		
		LOD <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	LOD <sup>b</sup> ( $\mu\text{g g}^{-1}$ )	RSD (20 $\mu\text{g L}^{-1}$ )	LOD <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	LOD <sup>b</sup> ( $\mu\text{g g}^{-1}$ )	RSD (20 $\mu\text{g L}^{-1}$ )
Cu	63	0.1	0.02	0.8	0.4	3.6	1.9
Ge	72	0.25	0.05	0.2	0.2	2.4	1.4
Mn	55	0.02	0.004	1.4	0.1	1.1	1.4
Mo	98	0.04	0.008	0.9	0.1	1.0	3.8
Ni	60	0.06	0.012	0.8	0.1	1.2	1.7
Sb	121	1.6	0.32	10.9	2.1	20.7	2.6
Sr	88	0.02	0.004	0.5	0.02	0.2	0.5
Ti	47	1.4	0.28	1.4	0.5	5.4	4.3
V	51	0.1	0.02	1.8	0.7	7.1	1.0

<sup>a</sup> Instrumental limit of detection.

<sup>b</sup> Procedure limit of detection.

compared with those obtained for microwave acid treatment. The recommended procedure involved low dilution allowing better detection limits (DL) for most analytes (between  $0.004 \mu\text{g g}^{-1}$  for Mn and Sr, and  $0.32 \mu\text{g g}^{-1}$  for Sb) with adequate precision as relative standard deviation (from 0.5% for Mo to 3.41% for Cu). The DLs were calculated as 3.3 times the standard deviation of a blank for ten replicate measurements ( $n = 10$ ) and the precision was calculated as per cent relative standard deviation (RSD%).

The obtained precisions were satisfactory, that is hardly attainable using conventional nebulizers for solutions with high carbon contents. In accordance with Boorn & Browner (1982), carbon deposition and the instability of the plasma were minimising. It can be corroborated by the low RSD values obtained for the different trace metals (see Table 1). Moreover, the IOC (2011) has established a maximum level of Cu of  $0.1 \mu\text{g L}^{-1}$  and according the results showed in Table 1, this method possesses enough detection capability which is not the case of the conventional method which is unsuitable to determine these values.

### 3.3. Analytical application and validation

As mentioned in Section 3.1, using a high performance introduction system with a cooled spray chamber enabled high solvent inputs to the ICP. However the nebulization efficiency is strongly dependent on the sample composition, and calibration against simple aqueous standards is not always reliable.

As a certified reference material of edible oils was not available and the metallic content of the lubricating oils was excessively high in comparison with the contents of the edible oils, recovery studies were carried out for the different samples (Table 2). In this

study, we evaluated the accuracy of the results by comparison ( $t$ -test, 95% confidence interval) with an independent sample treatment such as microwave digestion (Table 2). Adequate results were obtained (recoveries above 93%) with analyte addition method and Rh as internal standard for all analytes.

The proposed method for sample preparation using TMAH was applied for trace element analysis of edible oils available in Argentine markets (Table 3).

### 3.4. Correlation between variables

The range of concentrations found for each type of edible oil is shown in Table 3. The presence of Ge and Ti were observed in all analysed samples (except for one sample of almond oil). The presence of Cu only was observed in olive oils. Sb was detected in the majority of samples, except in corn oils. In contrast, Sr and high levels of V were found only in this last. Something similar happened with Mn and Ni in samples of corn oil; these elements were only found in a sample of almond and olive oil respectively. In addition, Mo was determined in one sample of sunflower oil.

The results of the analysis of the different edible oils were explored by using chemometric tools. PCA allowed a clustering of variables on the basis of mutual correlations, and a grouping of samples based on their similarities. Mean values ( $n = 3$ ) of the detected metals (Cu, Ge, Sb, and Ti) were used as variables to perform an exploratory analysis using PCA. The two first principal components (PC1 and PC2) retained 91.6% of the variability of the system. The results given in Fig. 2 showed a tendency of groupings between the samples of the same type of oil. PC1 seems to split oil samples between those of corn and the rest of the studied oils. The

**Table 2**  
Recoveries for spiked olive oil sample treated with TMAH (proposed method) and microwave digestion method.

Analyte	Proposed method				Microwave digestion method
	Base <sup>a</sup> ( $\mu\text{g g}^{-1}$ )	Added ( $\mu\text{g g}^{-1}$ )	Found ( $\mu\text{g g}^{-1}$ )	Recovery <sup>b</sup> (%)	Base <sup>a</sup> ( $\mu\text{g g}^{-1}$ )
Cu	$0.26 \pm 0.14$	0.5	$0.77 \pm 0.14$	101.5	$0.29 \pm 0.15$
Ge	$0.23 \pm 0.01$	0.5	$0.74 \pm 0.11$	100.1	$0.24 \pm 0.09$
Mn	<DL	0.5	$0.505 \pm 0.040$	101.0	<DL
Mo	<DL	0.5	$0.495 \pm 0.012$	99.0	<DL
Ni	$0.040 \pm 0.028$	0.5	$0.545 \pm 0.018$	101.1	$0.038 \pm 0.032$
Sb	$2.03 \pm 0.21$	0.5	$2.53 \pm 0.22$	99.5	$2.26 \pm 0.48$
Sr	<DL	0.5	$0.465 \pm 0.013$	93.0	<DL
Ti	$1.09 \pm 0.16$	0.5	$1.55 \pm 0.19$	93.6	$1.06 \pm 0.18$
V	$0.12 \pm 0.04$	0.5	$0.63 \pm 0.09$	101.2	$0.11 \pm 0.09$

<sup>a</sup>  $n = 3$ ; Confidence intervals as two standard deviation.

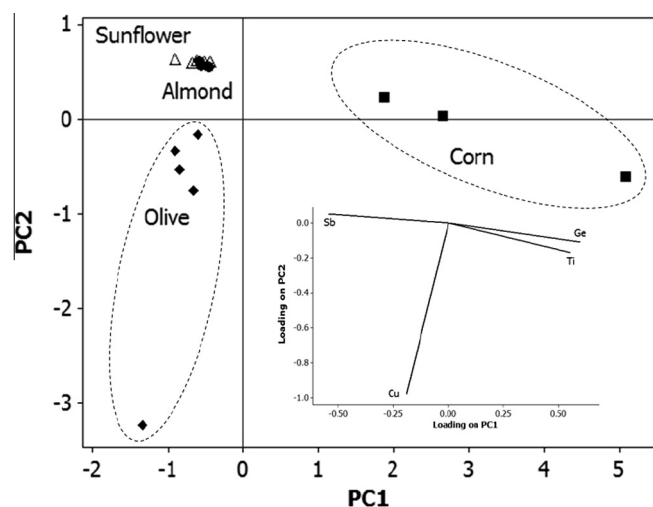
<sup>b</sup> Calculated as  $100 \times (\text{found} - \text{base})/\text{added}$ .



**Table 3**

Results obtained in edible oils available in Argentine market treated with TMAH (expressed in  $\mu\text{g g}^{-1}$ ), using matrix matching calibration with 15%v/v TMAH (confidence level 95%).

Oil	Cu	Ge	Mn	Mo	Ni	Sb	Sr	Ti	V
Almond	<DL	$0.16 \pm 0.01$	$0.009 \pm 0.002$	<DL	<DL	$1.47 \pm 0.05$	<DL	<DL	<DL
Almond II	<DL	$0.21 \pm 0.03$	<DL	<DL	<DL	$1.70 \pm 0.19$	<DL	$0.711 \pm 0.34$	<DL
Almond III	<DL	$0.19 \pm 0.02$	<DL	<DL	<DL	$1.57 \pm 0.05$	<DL	$0.867 \pm 0.51$	<DL
Corn	<DL	$0.73 \pm 0.06$	$0.157 \pm 0.014$	<DL	$5.151 \pm 1.471$	<DL	$0.061 \pm 0.016$	$1.815 \pm 0.71$	$21.56 \pm 7.26$
Corn II	<DL	$1.51 \pm 0.06$	$0.260 \pm 0.013$	<DL	$7.622 \pm 0.471$	<DL	$0.100 \pm 0.016$	$11.926 \pm 6.09$	$39.89 \pm 3.63$
Corn III	<DL	$0.98 \pm 0.06$	$0.254 \pm 0.014$	<DL	$7.222 \pm 0.423$	<DL	$0.081 \pm 0.012$	$3.761 \pm 1.14$	$29.76 \pm 2.54$
Olive	$0.39 \pm 0.02$	$0.16 \pm 0.02$	<DL	<DL	<DL	$1.33 \pm 0.28$	<DL	$0.367 \pm 0.03$	<DL
Olive II	$0.32 \pm 0.01$	$0.17 \pm 0.01$	<DL	<DL	<DL	$1.73 \pm 0.18$	<DL	$0.887 \pm 0.15$	<DL
Olive III	$0.21 \pm 0.01$	$0.17 \pm 0.01$	<DL	<DL	<DL	$1.45 \pm 0.25$	<DL	$0.582 \pm 0.08$	<DL
Olive IV	$1.11 \pm 0.04$	$0.18 \pm 0.02$	<DL	<DL	<DL	$1.62 \pm 0.27$	<DL	$0.621 \pm 0.28$	<DL
Olive V	$0.26 \pm 0.14$	$0.24 \pm 0.01$	<DL	<DL	$0.040 \pm 0.028$	$2.03 \pm 0.21$	<DL	$1.09 \pm 0.16$	$0.12 \pm 0.04$
Sunflower	<DL	$0.18 \pm 0.01$	<DL	$0.018 \pm 0.005$	<DL	$1.98 \pm 0.32$	<DL	$0.395 \pm 0.17$	<DL
Sunflower II	<DL	$0.16 \pm 0.01$	<DL	<DL	<DL	$1.44 \pm 0.10$	<DL	$0.334 \pm 0.04$	<DL
Sunflower III	<DL	$0.16 \pm 0.02$	<DL	<DL	<DL	$1.57 \pm 0.32$	<DL	$0.237 \pm 0.06$	<DL
Sunflower IV	<DL	$0.15 \pm 0.01$	<DL	<DL	<DL	$1.30 \pm 0.07$	<DL	$0.162 \pm 0.03$	<DL
Sunflower V	<DL	$0.17 \pm 0.03$	<DL	<DL	<DL	$1.79 \pm 0.57$	<DL	$0.868 \pm 0.19$	<DL
Sunflower VI	<DL	$0.17 \pm 0.02$	<DL	<DL	<DL	$1.63 \pm 0.40$	<DL	$0.925 \pm 0.02$	<DL



**Fig. 2.** Bivariate plot for the first two PCs. Samples are identified according to the type of oil. Inset: loadings plot for PC1 and PC2.

first ones showed always positive PC1 scores while the rest showed negative PC1 scores. Moreover, samples with high values of PC1 present high contents of Ge and Ti and low amounts of Sb. On the other hand, PC2 separated the olive samples from sunflower and almond oils. It was influenced by the content of Cu and Sb, which showed an inverse correlation. From this exploratory analysis it can be concluded that the content of trace metals is related to the provenance, type and category of oil.

#### 4. Conclusion

Samples of edible oils are properly solubilised with TMAH, enabling the introduction to the ICPMS using a microconcentric nebulizer operated at  $-5^\circ\text{C}$  with oxygen gas as auxiliary carrier. The sample preparation with TMAH can be an attractive alternative for routine analysis by ICPMS, considering mainly the multielement analysis capabilities of complex matrices with high carbon concentration, as oils. Furthermore, the proposed method is fast, simple, precise, accurate and less expensive. In addition, the achieved detection powers were higher than those reached with conventional microwave digestion. Variable amounts of Cu, Ge, Mn, Mo, Ni, Sb, Sr, Ti, and V in olive, corn, almond and sunflower oils were observed. PCA studies have been performed with Cu,

Ge, Sb, and Ti, observing correlations between the contents of these elements and the type of oil. In sum, valuable information could be obtained for edible oils allowing its classification according to elemental contents. Future studies on oils traceability and/or origin denomination may be carried out following the recommended procedure.

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