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The accurate direct elemental analysis of fats and oils is accomplished according to a dilution and shot analysis method

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Multielemental analysis of vegetable oils and fats by means of ICP-OES following a dilution and shot methodology

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The elemental analysis of vegetable oils as well as fats of animal origin through inductively coupled plasma optical emission spectroscopy, ICP-OES, according to a dilution and shot analysis method is reported for the first time. In order to introduce the diluted samples, a 5 μL sample volume has been injected into an air carrier stream and lead to a conventional pneumatic concentric nebulizer. A transient signal or peak has been obtained. The so-called high temperature torch integrated sample introduction system (hTISIS) has been used to lead the sample to the plasma and a conventional Cyclonic spray chamber has been taken for comparison purposes. Before performing the analysis of the selected samples, some critical variables such as the speed at which the sample plug was delivered to the nebulizer, the injected sample volume and the nebulizer gas flow rate have been optimized. The sample dilution factor has also been evaluated and the best performance has been obtained when samples have been 1:20 diluted with xylene as solvent. An accuracy study has been carried out in which the hTISIS has provided satisfactory results using an external calibration approach in which xylene based standards have been used. In contrast, the Cyclonic spray chamber causes matrix effects thus requiring the use of an alternative technique such as internal standardization or standard additions. In addition, the former system mitigates the impact of the analyte chemical form on sensitivity as it has been verified for silicon. Besides these two advantages, the hTISIS has also improved the analytical figures of merit over the Cyclonic spray chamber by a factor between 4 and 10 whereas limits of detection have been improved by a factor included within the 1.1 and 7.3 range. Compared to a method based on sample digestion and further ICP-MS detection, the present protocol is simpler, faster, it provides information about a higher number of elements and, in some cases, it affords lower limits of quantification while it gives rise to similar confidence intervals. The hTISIS has allowed the accurate determination of Al, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Si, Ti and V in solid fats as well as used and non-used liquid oils.

Introduction

Limited sources of fossil fuels have led to the production of renewable fuels, being biodiesel one of the most widely used. Biodiesel is generally produced by transesterification reactions from several feedstocks, such as edible vegetable oils (*e.g.*, palm, soybean, sunflower, coconut) or microalgae. However, the use of edible oils to produce biodiesel inevitably competes with food production. Therefore, the utilization of non-edible crops, animal fats and waste cooking oil for biofuel production are rapidly rising.^{1,2}

However, this kind of biodiesel feedstock contains metals and metalloids whose concentrations depend on the raw material, extraction procedures, catalyst, additives, physico-chemical refining processes, transportation and storage.^{3,4,5} A thorough control of these species is important for several reasons: (i) they can affect the

biodiesel stability; (ii) some of them are toxic and generate environmental concerns; (iii) others induce catalyst poisoning, clogging and fouling as well as corrosion in refining units; (iv) their presence may degrade the performance of the engine; and, (v) many elements are used as additives because they have anti-knock, metal deactivator, anti-rust, anti-icing, lubricant or detergent properties.⁶

Concentrations of some metals and metalloids even at the mg kg^{-1} level may cause all of the previously indicated problems. For this reason, sensitive and reliable techniques are required to carry out the elemental analysis of this kind of samples. Thus, some spectrometric techniques, such as flame atomic absorption spectrometry (FAAS),⁷ electrothermal atomic absorption spectrometry (ETAAS)⁸ and inductively coupled plasma optical emission spectrometry (ICP-OES)⁹ are normally used when the elemental concentration is included in the mg kg^{-1} range; whereas for elements present at lower concentrations ($\mu\text{g kg}^{-1}$), techniques with a better sensitivity are needed such as inductively coupled plasma mass spectrometry (ICP-MS).¹⁰ Apart from spectrometric techniques, electrochemical methods have also been applied.¹¹ Although atomic absorption spectrometric techniques are more tolerant to organic matrices than plasmas, they are mainly monoelemental techniques or only allow the simultaneous

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determination of a few elements. Moreover, they provide a narrower dynamic range than ICP techniques and detection limits are somewhat high (e.g., FAAS).³

Direct introduction of organic samples into an ICP is complex. These specimens have a wide variety of physical properties (*i.e.*, viscosity, density, surface tension and volatility) thus disturbing all the processes taking place in the instrument, from the solution nebulization and the aerosol transport to the analyte atomization and excitation in the plasma.¹² In order to overcome these limitations, different sample preparation methods have been developed, including ashing,¹³ open and closed wet digestion,¹⁴ microwave digestion,¹⁵ emulsification,¹⁶ microemulsification,¹⁷ liquid-liquid extraction,¹⁸ dispersive liquid-liquid microextraction¹⁹ and extraction induced by emulsion breaking.²⁰ Unfortunately, these procedures are generally time consuming, some of them require high volumes of reagents, hence inducing sample contamination or they promote volatile losses. A good approach is sample dilution²¹ with organic solvents. This procedure is fast, straightforward and easy-to-automatize. However, the degradation in the achievable limits of quantification when high dilution factors are required, the increase in the likelihood for sample contamination and the limited number of elements that can be determined dictated by the commercially available organic standards are among the main drawbacks of sample dilution.²² A critical point of this methodology is the solvent selection, because it must dissolve the sample, have a low volatility, low toxicity, be compatible with the instrument materials and not induce additional interferences. The solvents generally employed are xylene, toluene, kerosene, methyl isobutyl ketone (MIBK) and alcohols, such as ethanol, methanol or propan-1-ol.^{23,24,25}

Additional ways to overcome the problems associated to the introduction of organic solvents into the plasma are based on modifications of the sample introduction system. Thus, for instance, cooled spray chambers, desolvation systems or low sample consumption systems have been proposed.²⁶ Additionally, the so-called high temperature torch integrated sample introduction system (hTISIS) is a good alternative to carry out this kind of analysis. The system consists of a low inner volume single-pass spray chamber whose walls are heated by means of an electric resistance. Under optimized conditions, the analyte transport efficiency becomes virtually equal to 100% regardless of the sample matrix, thus improving the sensitivity provided by conventional devices and, simultaneously, reducing the extent of the matrix effects related to the spray chamber. Therefore, a universal calibration procedure can be implemented in which external calibration with a set of xylene based standards can be used for the analysis of all kind of organic samples.¹²

Up to now, the hTISIS has been employed to analyze light petroleum products (such as gasoline, kerosene and diesel) crude oil and its heavy fractions and biofuels by ICP-OES^{6,12,27,28,29} as well as ICP-MS.^{30,31} The goal of the present work was thus to develop a dilution and shot method for the multielemental analysis of oil and fat samples, used as feedstock for biofuel production. In order to accomplish this objective, the hTISIS was adapted to an ICP-OES system. In a first step, an optimization of the operating variables was undertaken. Dilution has been suggested to perform the analysis of oil samples.²³ Unfortunately, when a conventional sample introduction system is employed, matrix effects may be observed. Therefore, in the present work, the results encountered with the hTISIS have been compared against those for a Cyclonic spray chamber. Furthermore, because of its extended use, the data encountered when applying a sample digestion method have also

been compared against those found when directly analyzing a previously diluted sample.

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Finally, samples including vegetable crude as well as used oils and fats of animal origin were analyzed. All the studies were carried out by applying a sample air-segmented injection regime.

Experimental

Reagents and samples

Standards were prepared by dilution of a 100 mg kg⁻¹ multielemental stock solution (Conostan® S-21, SCP SCIENCE, Clark Grah, Baie D'Urfé, Canada) in xylene (Labbox Labware S.L., Vilassar de Dalt, Barcelona, Spain). Five different oil and fat samples were used to compare hTISIS and Cyclonic sample introduction systems. Two of them were liquid at room temperature (*i.e.*, used cooking oil, UCO and frying oil, HF) whereas the three remaining ones were solid under room conditions (*i.e.*, animal fat, GA, crude palm oil, CPO, and palm fatty acid distillate, PFAD). The rest of the samples, analyzed with both the hTISIS and also by a digestion procedure, corresponded to eleven samples (VO1-VO11). Their characteristics are included in Table 1.

Table 1. Characteristics of the vegetable oils and fats analyzed

VO1	Colza oil	Liquid
VO2	Bio-oil Sun pine	Solid
VO3	Tall oil	Liquid
VO4	Used cooking oil	Solid
VO5	Animal fat	Solid
VO6	Animal fat	Liquid-solid
VO7	Used cooking oil	Liquid-solid
VO8	Carinata oil	Liquid
VO9	Tall oil	Liquid
VO10	Tall oil	Liquid-solid
VO11	Corn oil	Liquid

Three different silicon compounds were taken in order to characterize the influence of the chemical form of this element on the ICP-OES sensitivity and on the accuracy of the results finally obtained. They were octamethyl cyclotetra-siloxane (compound A), dymethyloctyl chloro silane (Compound D) and hexamethyl disiloxane (compound R). Solutions containing 2 mg kg⁻¹ of silicon were prepared using xylene. Alternatively, independent aliquots of a given sample were spiked with each one of the compounds at the same silicon concentration (2 mg kg⁻¹).

Sample preparation and instrumental conditions

In order to perform multielemental analysis according to the dilution and shot method, liquid oil samples were manually shaken for 1 minute. After that, a given mass of the sample was weighed and properly diluted with xylene. In the case of the solid samples, they were heated for 15 min at 80 °C thus giving rise to a homogeneous and fluidized sample. To further ensure a good homogenization, the samples were heated twice for 5 minutes and shaken for 1 minute after every step.

An Optima 7300 DV Perkin-Elmer ICP-OES spectrometer (Überlingen, Germany) was used to measure the intensities. The selected operating conditions are collected in Table 2.

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Table 2. ICP-OES operating conditions.

Ar flow rates/ L min ⁻¹	Plasma: 15 Auxiliary: 1		
RF power/ kW	1.4		
Integration time/ s	0.1		
Sampling time/ s	0.4		
Replicates	6		
Emission lines/ nm	Al I 396.153	Cr II 267.716	Mo II 202.031
	Ar I 363.268	Cu I 327.393	Ni II 231.604
	Ba II 233.527	Fe II 238.204	Pb II 220.353
	C I 193.030	Mg II 280.271	Si I 251.611
	Ca II 315.887	Mg I 285.213	Ti II 334.940
	Cd I 228.802	Mn II 257.610	V II 290.880

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Additionally, some samples were digested using a microwave digestion system Start D (Milestone, Sorisole, Italy). Approximately 0.5 g (with a precision of ± 1 mg) of sample were transferred to a digestion vessel and then 6.5 mL of 65% HNO₃ (Labbox Labware S.L., Vilassar de Dalt, Barcelona, Spain) and 1 mL of 30% H₂O₂ (ScharLab S.L., Sentmenat, Barcelona, Spain) were added. Samples were digested at 200 °C for 30 min and final digests were transferred to plastic vessels and diluted to 20 g with Milli-Q water. The digests were finally analyzed through ICP-MS by means of and Agilent 7700 (Santa Clara, California) using external calibration and on-line addition of internal standards for quantification. The operating conditions are described elsewhere.³¹

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Air segmented analysis and sample introduction systems

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In order to perform the analysis, the so-called air segmented injection methodology was applied. According to this principle, the peristaltic pump (Perimax 16 antiplus, Spetec, Erding, Germany) aspirated air continuously at a controlled rate. Air was thus delivered to the nebulizer at a low flow rate that did not impact negatively the plasma performance. The estimated flow rate was on the order of 30 – 50 µL min⁻¹ depending on the pump speed rate. A 5 µL sample volume was measured with the help of an automatic micropipette (Eppendorf, Hamburg, Germany). Afterward, the plastic tip of the pipette was manually adapted to the 0.25 mm ID contour flared end of the solva pump tubing (Glass Expansion, Melbourne, Australia). Then, the measured volume was aspirated and driven towards a conventional glass pneumatic concentric nebulizer TR-30-A1, (Meinhard® Glass Products, Santa Ana, USA). Transient signals were obtained according to this methodology and the peak height was taken as analytical parameter. According to this methodology, sample dispersion in condensed state was avoided, because the carrier stream was simply air.³² Furthermore, the introduction of air between consecutive injections incorporated a small amount of oxygen and, hence, problems linked to the formation of soot deposits were mitigated.

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The hTISIS is a custom made sample introduction system, not yet commercially available. In the present study, it contained a 9 cm³ inner volume glass-made single-pass spray chamber. A copper coil was wound around the chamber and its temperature was set by means of a temperature controller (Design Instruments, Barcelona, Spain). For the sake of comparison, a 40 cm³ Cyclonic spray chamber was also employed.

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Statistical treatment

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The QC/QA assessment was performed by applying the F-test in order to be able to evaluate statistical differences in terms of variance between two given data sets. When the variance was considered as statistically comparable, the statistical differences were evaluated by means of the *t-Student* test. In the opposite case, Equation 1 was applied in order to compare the calculated with the determined *t* value. Equation 2 provided the mean for calculating the degrees of freedom.

Equation 1

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

Equation 2

$$\text{Degrees of freedom} = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\left(\frac{s_1^4}{n_1^2(n_1-1)} + \frac{s_2^4}{n_2^2(n_2-1)}\right)}$$

where *x* was the mean value, *s* was the standard deviation, *n*₁ and *n*₂ were the number of replicates for the two methods under comparison.

Results and Discussion

In a first place, the performance of the high temperature system was characterized. Afterward, samples were analyzed according to different schemes. The oils and fats tested in the present work induce problems, particularly related with the accuracy of the determinations. First, the methods applied so far have drawbacks linked to the time consumption, sensitivity degradation, losses of volatiles or sample pollution; second, unless hydrofluoric acid is used, sample digestion does not provide information of important elements, such as silicon, for instance;^{15,18} and, third, there is a lack of studies giving information about the multielemental content of this kind of non-edible raw materials.

Studies on aerosol transport and plasma thermal state

Because of the sample introduction regime corresponded to the air segmented mode, transient signals were obtained throughout this work. Before performing the analysis of the different samples, preliminary studies related to the characterization of the impact of the samples on the plasma and the sample introduction performance were undertaken. These studies dealt with: (i) the measurement of the carbon emission line what provided information about the physical form of the aerosol reaching the plasma, and; (ii) the measurement of the argon emission intensity and the magnesium ionic to atomic net emission intensity, since both parameters gave us indication of the plasma thermal state.

Carbon emission intensity

In order to get more insight on the behavior of the solvent and sample main component with the two sample introduction systems evaluated, the carbon emission signal was registered versus time. According to previous studies related to the analysis of non-volatile organic samples,⁶ the hTISIS temperature was set at 400 °C. Under these conditions, high analyte transport efficiencies were achieved. However, in the previous study, the performance of the carbon signal was not evaluated. Therefore, as the analytical signal confirmed, the

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behavior of the aerosol was expected to be a virtually complete evaporation before its introduction into the plasma. In order to test the aerosol fate in the hTISIS chamber, the carbon emission intensity was registered.

Representative examples of the obtained peaks for a random oil sample (VO11) are shown in Figure 1. The transient signals for carbon are superimposed with those measured for an analyte (*e.g.*, Si). The two evaluated sample introduction systems are included. First it may be observed that, for the two devices, the carbon peaks were wider than those for the analyte. It must be considered that silicon was only transported to the plasma in the form of solid particles or very small droplets. Carbon, instead, could be delivered to the excitation cell in both liquid and vapor forms.

For the Cyclonic spray chamber (Figure 1.a) the carbon signal, measured when the silicon peak was obtained (see grey area in Figure 1.a), was likely the result of the delivery of liquid and vapor solvent to the plasma. Therefore, the carbon signal gave an indication of the physical state of the solvent. In fact, once the Si signal reached the background level, the introduction of aerosol into the plasma ceased. Consequently, the signal for carbon was due to its introduction as a vapor (see orange region in Figure 1.a). Accordingly, it could be quite positively concluded that, once the aerosol was generated by the nebulizer and introduced into the spray chamber, a fraction of the droplets impacted against the chamber walls. The analyte remained retained inside the chamber whereas the solvent evaporated slowly from there being introduced into the plasma and providing a steeply decreasing signal.

The behavior found in the case of the hTISIS operated at high temperature (Figure 1.b) was qualitatively similar, but some differences were clearly evidenced with respect to the Cyclonic spray chamber. In a first instance, it was observed that carbon signal was saturated. Therefore, the maximum of the peak was not observed, thus giving rise to the carbon curve shown in Figure 1.b. By comparing the x-axis of both figures (a and b), it was clearly found that the processes occurring in the case of the hTISIS took place much more quickly than when the Cyclonic spray chamber was used. This was obviously due to the high temperature set and the low inner volume of the single pass spray chamber (*i.e.*, 9 cm³) for the former device. These results also led to the conclusion that, with oil samples, although a high temperature was set, a small fraction of the aerosol droplets could impact against the chamber because they were moving at high velocities. However, an additional reason will be latter argued in link with the amount of oxygen delivered between two consecutive injections.

Argon emission intensity

Once the behavior of the solvent was characterized, attention was paid to the plasma thermal state. The argon emission intensity helped to understand the impact of the sample on the global ability of the plasma to generate high energy argon particles. Argon positive peaks were obtained, both for the hTISIS and the Cyclonic spray chamber, what implied an enhancement in the plasma thermal state. This was interesting because, contrarily to what could be expected, the plasma became more robust when the sample reached it. Several explanations could be given. Among them, the plasma thermal pinch that consisted in the reduction of the plasma volume when the sample plug reached it.³³ As the supplied power was constant, the energy density in the plasma increased.^{34,35}

Magnesium ionic to atomic ratio

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Another parameter giving indication of the plasma thermal state is the magnesium ionic to atomic net emission intensity ratio.³⁶ In the present study, the magnesium ratio was calculated by dividing the intensity values obtained at the peak maximum. The impact of the sample introduction system on the plasma ionization capability was clear. When the hTISIS was used, the high temperature supplied together with the fact that the peak was narrower than in the case of the Cyclonic chamber, led to a higher instantaneous solvent plasma load. This was obviously the main reason for the decrease in the MgII/MgI ratio. It was noticed that this ratio was close to 6.1 and 7.8 for the hTISIS and the Cyclonic spray chamber, respectively.

Figure 1. Peaks obtained for carbon (red lines) and silicon (blue lines) for a random oil sample (VO11). (a) Cyclonic spray chamber; (b) hTISIS operated at 400 °C. Sample dilution factor, 1:20.

Optimization of operating conditions

In order to increase the sample sensitivity, simultaneously lowering the peak width, in previous reports the pump speed was kept at a rather high value (*c.a.*, 350 rpm).⁶ However, this could result in a reduction of the plasma excitation power with respect to low sample plug delivery flow rates. In the present work, the pump speed was systematically evaluated for the first time in air segmentation. This variable precluded both the peak shape and height. It was observed that, for the hTISIS, an increase in the pump speed had a small effect on the peak height (Figure 2.a). This trend was unexpected and, in order to understand it, the peak width was evaluated. As it may be observed from Figure 3, the peak width did not significantly change in spite to the fact that the liquid flow rate was increased by a factor of three. In absence of sample dispersion in liquid phase, *i.e.*, the sample was injected in an air stream, these results highlighted the

importance of the aerosol dispersion inside the chamber.³⁷ For a device having a higher inner volume (such as the Cyclonic chamber) Figure 2.b reveals that an increase in the pump speed up to 300 rpm yielded a growth in the peak height. This point was attributed to the decrease in the peak width (see Figure 3).

Another studied variable was the nebulizer gas flow rate. Taking into account the impact that could have an excessively high mass of organic solvent on the plasma characteristics, low values of this parameter were set. The gas flow rate study was focused on the 0.07 to 0.2 L min⁻¹ range. It was encountered that the higher this variable, the lower the ICP-OES sensitivity. Possible reasons are the decrease in the aerosol heating efficiency inside the hTISIS chamber, the increase in the load of cold gas reaching the plasma central channel and the shortening in the aerosol residence time inside the excitation cell. Because the RSD was also lower at 0.07 and 0.1 L min⁻¹ than for the remaining tested flow rates, it was finally concluded that a certainly low value (0.1 L min⁻¹) was appropriate for further studies.

The sample injected volume was varied from 2 to 10 µL. In this case, the obtained data indicated a steep increase in the peak height. It was observed that the peak height was proportional to the injected sample volume up to 5 µL, thus indicating that the percentage of sample reaching the plasma was the same for this volume range. However, above 5 µL, the linear correlation disappeared, likely because the peaks became less defined under these conditions, and a stationary signal appeared at their tops. Meanwhile, the precision expressed as the relative standard deviation was better above 5 µL and, in order to avoid plasma degradation effects, this was the selected volume.

Figure 2. Effect of the pump speed on the manganese peak height, the hTISIS operated at 400 °C heating temperature (a) and the Cyclonic spray chamber (b).

Figure 3. Effect of the pump speed on the manganese peak width for the hTISIS operated at 400 °C heating temperature and the Cyclonic spray chamber.

Effect of the sample dilution factor

The dilution factor may affect both sensitivity and matrix effects. Figure 4 shows the silicon intensity measured using the Cyclonic spray chamber and the hTISIS as a function of the dilution factor for five different samples. Besides its obvious interest for the fuel industry, silicon is a difficult element because it occurs under very different chemical forms, each one providing different sensitivities, and it is difficult to put in solution.³¹ Hence, additional methodologies, such as sample dilution and shot analysis, must be developed. It should be mentioned that the samples were spiked at 2.5 mg kg⁻¹. The results in Figure 4 indicated that, depending on the sample, the net signal either did not change or slightly increased as the sample became more diluted. This fact could be explained by taking into account that an increase in this variable led to a lowering in viscosity and a growth in volatility of the obtained solutions. In the analysis of non-spiked samples, both facts promoted the transport of solution to the plasma, thus counterbalancing the decrease in analyte concentration.

An interesting observation was that for the hTISIS the sensitivity was not dependent on the sample nature for the 1:20 dilution factor. This fact meant that the influence of the matrix in terms of ICP-OES sensitivity was negligible under this situation. Therefore, the 1:20 dilution factor was selected as the most appropriate one.

The role of air in segmented injection under optimum conditions

The optimum conditions (*i.e.*, 5 µL injected sample volume, 200 rpm pump speed rate, 0.1 L min⁻¹ nebulizer gas flow rate and 1:20 dilution factor, together with the 400 °C hTISIS temperature) found for silicon were also the best ones in terms of sensitivity for all the elements studied in the present work.

Under these operating conditions, it was verified that the hTISIS was able to work in a stable fashion for short and long periods of time. Thus, typically, the RSD(%) peak height found for a 1 mg kg⁻¹ multielemental standard remained below 6% for six consecutive injections. Meanwhile, this parameter was lower than 10% for three sets of experiments performed during an eight-hours period of time.

It is worth to mention that, with the evaluated setups, no oxygen was added to the aerosol stream. Even under these conditions the plasma remained stable. This observation could be assigned to the work under the air segmented injection approach. In fact, it was found that soot deposits were quickly produced neither on the injector nor in the torch. It was thus possible to perform

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measurements during a full working day with no need for replacing any component of the system.

Under the specified optimum conditions, the volume of air aspirated by the peristaltic pump per minute was 40 μL what corresponded to 3.5×10^{-7} moles of oxygen under normal conditions. By considering the carbon mole number injected in the case of xylene standards, for instance, (*c.a.*, 3.7×10^{-5}) and the carbon oxidation reaction:

It was concluded that the amount of oxygen delivered was lower than that required for complete carbon oxidation. However, only a fraction of this carbon was potentially able to produce soot deposits because a big amount of this element was injected through the plasma central channel. I was decided, thus to establish a 1-minute delay time between two consecutive injections that yielded a sample throughput approached to 30 h^{-1} .

Therefore, an alternative explanation to the width of the peaks shown for carbon with respect to that for the analyte (Figure 1) was that a fraction of this element initially deposited somewhere in the torch was released as a result of its reaction with oxygen.

Figure 4. Silicon intensity found for the Cyclonic spray chamber (a) and hTISIS operated at 400 °C (b) for five different dilution factors. UCO: Used cooking oil; HF: frying oil; PFAD: palm fatty acid distillates; CPO: crude palm oil; GA: animal fat. Samples were spiked at a 2.5 mg kg^{-1} multielemental concentration.

Comparison of the hTISIS, the Cyclonic spray chamber and the digestion method

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A comparison between the two evaluated sample introduction systems was established in terms of sensitivity and limits of detection for oily samples. The data demonstrated that the hTISIS afforded sensitivities from roughly 4 to 10 times higher than the Cyclonic device. In the case of silicon (Figure 4), for example, this factor could be as high as 40.

Furthermore, the peak width was also lower when the high temperature system was used. The reduction factor in terms of this parameter was close to three (Figure 3). The hTISIS was thus a more suitable design for the work with organic microsamples.

Limits of detection, LOD, and limits of quantification, LOQ, were calculated according to:

$$\text{LOD} = \frac{3 s_b}{S} \quad \text{Equation 4}$$

$$\text{LOQ} = \frac{10 s_b}{S} \quad \text{Equation 5}$$

where s_b was the standard deviation corresponding to twenty consecutive measurements of the background and S the sensitivity obtained for the 0.25 mg kg^{-1} standard concentration. The obtained results are gathered in Table 3 for the hTISIS and the Cyclonic spray chamber. It was found that both parameters were significantly lower for the former device. The improvement factor varied strongly with the element and it was contained between 1.1 (Pb) and 7.3 (Ba).

The LOQs in parenthesis (Table 3) were obtained from a standard, taking into account that the samples were 1:20 diluted prior their analysis, the included figures had to be multiplied by 20 in order to obtain realistic analyte concentrations that could be actually determined.

The limits of detection and quantification obtained according to a protocol based on the sample digestion are also summarized in the two last columns of Table 3. These parameters were calculated by applying equations 4 and 5 but, in this case, s_b was the standard deviation of the ICP-MS signals for the solutions obtained after the blank digestion. Furthermore, the sample dilution factor (*i.e.*, 40) was taken into consideration. Therefore, the obtained data gave indication of the lowest concentration that could be determined in the sample (*i.e.*, method LOD and LOQ). In order to establish a fair comparison, the LOQs obtained with the hTISIS were multiplied by the sample dilution factor (*i.e.*, 20). Several interesting observations were made, because, in spite of the fact that the high temperature system was adapted to an ICP-OES spectrometer, for three elements (Al, Fe and Mg) LOQs were lower for the hTISIS than when a digestion based procedure. Furthermore, Cr, Mn and Ti provided similar LOQs with both methodologies (*i.e.*, dilution and ICP-OES shot analysis using the hTISIS and microwave digestion and ICP-MS determination). Additionally, Ca and Si were not analyzed because of isobaric and interferences and poor solubilization, respectively. Finally, for Ba, Cd, Cu, Mo, Ni, Pb and V better LOQs were obtained when applying ICP-MS method than for the ICP-OES one.

Recoveries

Recovery studies allowed verifying the accuracy of the method based on the use of the hTISIS. Samples were spiked with the Conostan® multielemental solution and then analyzed together with a standard prepared in xylene having a concentration corresponding to the spiked one. Then, the following equation was applied:

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Table 3. Limits of detection, LOD, and limits of quantification, LOQ, found for the hTISIS, the Cyclonic spray chamber and the digestion method.

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Element	LOD/ $\mu\text{g kg}^{-1}$		LOQ/ $\mu\text{g kg}^{-1}$		Ratios Cyclonic/hTISIS	Microwave digestion	
	hTISIS	Cyclonic	hTISIS*	Cyclonic*		LOD/ $\mu\text{g kg}^{-1}$	LOQ/ $\mu\text{g kg}^{-1}$
Al	1.6	3.1	5.0 (100)	10 (200)	4.2	250	850
Ba	0.35	2.5	1.2 (24)	8.5 (170)	7.3	3.4	11
Ca	0.60	1.1	2.0 (40)	3.8 (76)	1.9		
Cd	2.6	8.9	8.8 (176)	30 (600)	3.4	2.2	7.4
Cr	0.59	1.64	2.0 (40)	5.4 (108)	2.7	11	35
Cu	0.94	1.64	3.1 (62)	5.5 (110)	1.7	5.2	17
Fe	0.86	3.1	2.9 (58)	11 (220)	3.7	72	240
Mg	0.16	0.64	0.55 (11)	2.1 (42)	3.9	16	53
Mn	0.20	0.69	0.66 (13)	2.3 (46)	3.5	2.4	8.0
Mo	4.1	5.7	14 (280)	19 (380)	1.4	1.9	6.2
Ni	2.7	4.9	8.9 (178)	16 (320)	1.8	5.2	17
Pb	18	20	59 (1180)	67 (1340)	1.1	3.0	9.9
Si	0.91	1.3	3.0 (60)	4.2 (84)	1.4		
Ti	0.21	0.43	0.7 (14)	1.4 (28)	2.1	4.8	16
V	0.81	1.2	2.7 (54)	4.0 (80)	1.5	0.6	2.0

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*The figures in parenthesis show the LOQ in the sample. In order to obtain it, the LOQ has been multiplied by 20 (i.e., the sample dilution factor) thus giving rise to the method LOQ.

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$$\text{Recovery (\%)} = \frac{I_{\text{spiked sample}} - I_{\text{non-spiked sample}}}{I_{\text{standard}} - I_{\text{xylene}}} \cdot 100 \quad \text{Equation 6}$$

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where $I_{\text{spiked sample}}$ and $I_{\text{non-spiked sample}}$ were the signal intensities of the spiked sample with 1 mg kg^{-1} of Conostan® CS-21 multielemental standard and the non-spiked one, respectively; I_{standard} was the intensity of a Conostan® 1 mg kg^{-1} solution using xylene as the solvent; and I_{xylene} was the blank intensity.

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Figure 5 plots the recovery results for the elements determined by using the two sample introduction systems. The elements determined were selected taking into account both their concentration in the samples and the procedural limits of detection for the Cyclonic spray chamber. In this case, Mo, Pb and Ni were not included, because the low sensitivity and the poor definition of the peaks found in the case of the Cyclonic spray chamber. It was found that this chamber provided recoveries significantly lower than 100%. The matrix effect could be assigned to the lower volatility of the diluted samples with respect to the standards used for external calibration. As a result, the sensitivity was lower in presence than in absence of samples, thus giving an underestimation of the analyte concentrations. Meanwhile, the hTISIS, working at 400°C afforded recoveries very close to 100%. These results were in agreement with those previously shown in Figure 4 for silicon and the 1:20 dilution factor. Therefore, with this device, changes in the emission intensity induced by a modification in the sample matrix were overcome. This led to the conclusion that, in the case of the hTISIS, external calibration with xylene based standards could be used for the analysis of different fatty samples with good accuracy.

Figure 5. Recoveries for a set of twelve elements and five fatty samples. (a) Cyclonic spray chamber; (b) hTISIS operated at 400°C . UCO: Used cooking oil; HF: frying oil; PFAD: palm fatty acid distillates; CPO: crude palm oil; GA: animal fat.

Dilution and shot analysis versus microwave digestion

An additional experiment was carried out in order to further test the reliability of the dilution and shot analysis method. In this case, eleven vegetable oil and animal fat samples were analyzed and the obtained concentrations were compared against those provided by the digestion method. The diluted digests were analyzed by means of ICP-MS using a conventional sample introduction method. Blanks containing only nitric acid and water were also digested and analyzed.

Table 4 compares the obtained concentrations. It may be observed that, for the evaluated situations, similar data were provided by the two studied methodologies. Statistical tests given by Equations 1 and 2 revealed that the results were not significantly different ($\alpha = 0.05$, $n_1 = 6$, $n_2 = 3$) for most of the cases, Table 4. Only in 9 out of the 55 evaluated cases, statistically different results were provided by the two methods (see the figures in bold characters).

It should be noted that with the dilution method it was possible to have access to more data than when the samples were digested because of the obvious degradation in the limits of detection for the latter method. According to the information given previously, when samples were digested, they were diluted by a factor of 1:40. Moreover, the concentrations determined for many elements in the digestion blanks were similar to those measured in the digests for the samples what revealed sample contamination from the MW reactors. Furthermore, it was found that the concentrations for elements such as Ba, Cd, Cu, Ni, Pb, V, Ti, (not included in Table 4) were systematically lower when the samples were digested with respect to the data provided by the hTISIS. Mo was not detected with the digestion method. These facts were likely due to either the incomplete digestion of these elements or the loss of volatile species (e.g., Cd).³⁸ Ca, in turn, was subject to isobaric ICP-MS interferences and, hence, was not determined for the digestion procedure. In addition, for some elements (e.g., Ni) high blanks were obtained. As a result, reliable data were only obtained for five elements when the digestion method was applied.

A comment should be added as regards silicon quantification. The digestion method had a clear limitation, because it was necessary to add hydrofluoric acid in order to determine this element. However, besides safety concerns when handling this acid, the components of the sample introduction systems were all made of glass and, hence, it was not possible to introduce solutions containing HF. This is why, the digestion of the samples was carried out with a mixture of nitric acid and hydrogen peroxide. Obviously, an accurate dilution and shot methodology would be more appropriate to perform the analysis of this kind of samples.

Comparison between external calibration and single point standard addition

Further evaluation of the accuracy when using the hTISIS was based on the analysis of eleven vegetable oil and fat samples according to two methodologies: (i) external calibration in which the emission intensities were measured for a set of xylene based standards; and, (ii) single point standard addition^{39,40} that consisted of the measurement of the signal for the blank, the sample and the same sample spiked with a multielemental standard. Expectedly, the concentrations provided by the second method could be considered to be close to the actual ones, because this method compensated for the existing matrix effects.⁴¹ The concentration ratios obtained with

the two methodologies are recovered in Figure 6 for the elements present in the samples at concentrations above the method LOD (see Table 3). The target value was, in this case, the unity (no differences in both sets of concentrations). The light gray horizontal band in Figure 6 corresponded to a $\pm 10\%$ tolerance value. Note that the RSD of the relative parameter was lower than 20%. Therefore, the results suggested that both selected quantification methods provided similar performances (i.e., concentration ratios were not statistically different, $\alpha = 0.05$, $n_1 = 6$, $n_2 = 6$, with respect to the tolerance level) in most of the situations studied and, hence, the dilution and shot analysis method based on the use of the hTISIS was suitable for multielemental analysis of this kind of samples.

Impact of the silicon chemical form

As it has been previously observed, silicon was found in the fatty samples analyzed. Silicon is a difficult element to analyze according to a digestion based method because it is necessary to add hydrofluoric acid. Thus, a method based on the sample dilution and its further analysis would allow obtaining quantitative data of this element in a quick and accurate way. It has been indicated that the chemical nature of this element may have a direct impact on the instrument performance.⁴² Therefore, an evaluation of the nature of the silicon compound present in the sample was done in terms of sensitivity. Three different compounds were taken: two siloxanes (codified as A and R) and a silane (compound D). According to previous studies, these three species exerted the most important influence on sensitivity when a conventional sample introduction system was used.⁴³

Calibration lines were obtained using the Cyclonic spray chamber or the hTISIS operated at 400 °C for standards containing silicon concentrations from 0.5 to 4.0 mg kg⁻¹. The slopes of the calibration lines did not differ significantly taking values of 53300 $\pm$ 1000, 53000 $\pm$ 1300 and 55000 $\pm$ 1700 cps (mg kg⁻¹)⁻¹ for compound D, A and R, respectively.

Additional studies were carried out in which an oil sample (VO11) was spiked with several silicon species at a given concentration (i.e., 2 mg kg⁻¹). The analysis was performed using compound D in the standards. The obtained recoveries were 95 $\pm$ 6, 97 $\pm$ 4 and 105 $\pm$ 2 % when the added compounds were A, D and R, respectively. Besides, non-spiked VO11 was analyzed using standard addition. In this case, the sample was spiked with silicon using one of the three compounds in each one of the assays. Determined silicon concentrations in the sample were 32.4 $\pm$ 5.3, 31.5 $\pm$ 5.1, and 30.0 $\pm$ 4.5 mg kg⁻¹ when the standards contained compound A, D and R, respectively. Meanwhile, the use of a set of standards prepared from a Conostan® stock solution yielded a concentration of 35.1 $\pm$ 1.6 mg kg⁻¹ that was in a quite good agreement with the previously mentioned data. These results collectively confirmed for the first time that the hTISIS was perfectly indicated to overcome effects associated to the modification in the chemical nature of silicon when oil samples are analyzed.

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Table 4. Elemental concentrations in mg kg⁻¹ (expressed as mean $\pm \frac{ts}{\sqrt{n}}$)* for three different oil samples using the dilution and shot analysis method and a microwave digestion procedure.

Element	Method	VO1	VO2	VO3	VO4	VO5	VO6	VO7	VO8	VO9	VO10	VO11
Al	hTISIS	< 0.10	13.4 $\pm$ 1.6	1.2 $\pm$ 0.2	6.1 $\pm$ 0.6	0.70 $\pm$ 0.04	4.4 $\pm$ 0.3	1.1 $\pm$ 0.2	0.47 $\pm$ 0.09	1.1 $\pm$ 0.2	18.4 $\pm$ 1.9	1.6 $\pm$ 0.2
	Digestion	< 0.85	15 $\pm$ 3	1.2 $\pm$ 0.3	16 $\pm$ 3	< 0.850	4.4 $\pm$ 0.9	0.83 $\pm$ 0.12	1.0 $\pm$ 0.7	1.10 $\pm$ 0.09	19 $\pm$ 2	1.34 $\pm$ 0.15
Cr	hTISIS	0.13 $\pm$ 0.02	1.02 $\pm$ 0.14	0.10 $\pm$ 0.02	0.15 $\pm$ 0.02	0.27 $\pm$ 0.02	0.24 $\pm$ 0.02	0.35 $\pm$ 0.03	0.11 $\pm$ 0.02	0.33 $\pm$ 0.02	0.46 $\pm$ 0.07	0.44 $\pm$ 0.07
	Digestion	0.128 $\pm$ 0.012	0.82 $\pm$ 0.15	0.134 $\pm$ 0.018	0.20 $\pm$ 0.18	0.205 $\pm$ 0.018	0.089 $\pm$ 0.018	0.19 $\pm$ 0.09	0.063 $\pm$ 0.012	0.365 $\pm$ 0.009	0.134 $\pm$ 0.012	0.56 $\pm$ 0.05
Fe	hTISIS	< 0.058	26.6 $\pm$ 1.6	0.28 $\pm$ 0.08	11.9 $\pm$ 1.3	1.68 $\pm$ 0.14	9.7 $\pm$ 0.5	7.4 $\pm$ 0.2	0.20 $\pm$ 0.05	0.58 $\pm$ 0.08	12.0 $\pm$ 1.5	5.7 $\pm$ 0.8
	Digestion	< 0.240	27 $\pm$ 3	0.24 $\pm$ 0.18	23 $\pm$ 10	2.8 $\pm$ 0.2	9.2 $\pm$ 0.6	9.6 $\pm$ 0.6	0.22 $\pm$ 0.12	0.67 $\pm$ 0.18	30 $\pm$ 5	6.1 $\pm$ 0.6
Mg	hTISIS	< 0.011	15.0 $\pm$ 0.5	1.29 $\pm$ 0.14	4.3 $\pm$ 0.6	0.59 $\pm$ 0.10	0.67 $\pm$ 0.08	0.85 $\pm$ 0.10	< 0.011	0.7 $\pm$ 0.4	5 $\pm$ 2	4.8 $\pm$ 0.4
	Digestion	< 0.053	13.5 $\pm$ 1.5	0.7 $\pm$ 0.6	5.3 $\pm$ 0.5	0.89 $\pm$ 0.15	0.7 $\pm$ 0.5	0.8 $\pm$ 0.5	< 0.053	0.5 $\pm$ 0.2	8.7 $\pm$ 1.5	4.9 $\pm$ 0.6
Mn	hTISIS	< 0.013	34.6 $\pm$ 1.6	0.95 $\pm$ 0.07	< 0.013	0.09 $\pm$ 0.04	0.12 $\pm$ 0.04	0.26 $\pm$ 0.06	< 0.013	0.27 $\pm$ 0.06	0.16 $\pm$ 0.06	< 0.013
	Digestion	< 0.008	40 $\pm$ 5	0.78 $\pm$ 0.06	< 0.008	0.05 $\pm$ 0.02	0.085 $\pm$ 0.012	0.07 $\pm$ 0.03	< 0.008	0.21 $\pm$ 0.06	0.22 $\pm$ 0.03	< 0.008

* n = 6 for the hTISIS and 3 in the case of the sample digestion

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Figure 6. Comparison between the concentrations found according to the external calibration method against those provided by a single point standard addition for vegetable oils and fats. hTISIS operated at 400 °C heating temperature.

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Analysis of oil and fat samples

Because all the assays carried out suggested that the hTISIS provided accurate results, oils and fats were analyzed using this accessory in combination with external calibration based on xylene multielemental solutions. A total of sixteen samples were analyzed. The quantitative results are included in Table 5 and Table 6. For the sake of comparison, data obtained using the Cyclonic spray chamber are also included in Table 5. The statistical test described in the experimental section revealed that, only for ten situations (see bold characters in Table 5), both systems provided statistically similar concentrations ($\alpha=0.05$, $n_1=n_2=6$). Possible discrepancies between the data found for the hTISIS and the reference system were attributed to the lack of accuracy encountered for the Cyclonic device. Furthermore, this table also reveals that concentrations values were obtained for eight out of fifteen elements. This was because the Cyclonic chamber (and, in some cases, the hTISIS) did not provide any distinguishable signal from the blank.

Iron content was especially high in the case of used cooking oil (Table 5) as well as several vegetable oils and fats (Table 6). This element may migrate from components made of stainless steel. Another element present in oil samples at a remarkable concentration was silicon. Its concentration ranged from 2.6 to around 100 mg kg⁻¹. No previous data regarding multielemental analysis involving this element have been reported in the literature. Barium is another element found at the mg kg⁻¹ level in samples such as used cooking oil and frying oil as well as in 8 out of 11 samples.

Magnesium was found in virtually all the samples analyzed at contents included within the 0.5 to 15 mg kg⁻¹ range. Previously published studies report results included in this range (Table 7). Cadmium is generally present at sub-ppm levels in many of the analyzed samples which is also in agreement with previous reports (Table 7). Only two samples, VO2 and VO7, contained cadmium concentration at values above 1 mg kg⁻¹. Generally, copper can be present in oil samples of vegetal origin because it may be used as a pesticide. This could be reason argued to try to explain the high concentrations of this element encountered for some samples (Table 6) as compared to the previously published results (Table 7).

Elements such as Mn, Al, Cr, Pb, Ti and V were also found in vegetable oils whose provenance can be ascribed to the assimilation of the plant and/or the pollution during the oil production and processing. The role of the elements found in the analyzed samples is of high importance in terms of the application of oils and fats to

the fuel production. Some of them (*e.g.*, Ca, Cu, Fe, Mg, Mn, Ni or Pb) may promote the oil degradation. This would have a direct consequence on the quality of biodiesel because the products of degradation reactions may cause fuel filter plugging, injector fouling, corrosion and deposit formation in the engine and fuel system, reducing the lifetime and the engine efficiency. In addition, after the combustion process, metals released into the air, may degrade its quality. Moreover, elements such as V are highly active as catalyst poisons and cause an increase in the emission of exhaust gases (CO, CO₂, N₂O...) as well as particulate materials. Other elements (*i.e.*, Al, Ca, Cr, Cu, Mg, Mn, Ni or Si) are incorporated to the final biodiesel as additives.^{1,43,44}

Finally, the obtained elemental concentrations for the analyzed samples were compared against those previously indicated in the literature (see Table 7). By evaluation of these results, it was concluded that the data found in the present work were in general agreement with those already published, although with the method developed in the present study it was possible to obtain quantitative information of a higher number of elements. This last point being only limited by the number of elements present in commercially available standards.

Conclusions

The rapid and accurate analysis of vegetable oils and fats of animal origin through ICP-OES is possible by means of the use of the hTISIS upon optimizing variables such as the sample delivery rate, injected sample volume and sample dilution factor. Thanks to the mitigation of the matrix effects when using the high temperature system, it is possible to perform a calibration based on the use of a set of xylene based multielemental standards. Besides, the impact of the silicon chemical form on sensitivity can be neglected. Further studies could be extended to the evaluation of this effect for elements others than silicon.

Moreover, the injection of a small sample volume in an air carrier stream minimizes the sample consumption and, even more important, minimizes the generation of toxic wastes. Both facts make it easier to manage an elemental analysis laboratory.

This work complements some existing ones for heavy as well as light petroleum products and approaches the hTISIS/ICP-OES to a universal technique useful for the multielemental analysis of organic samples without taking into account the contribution of the sample and analyte nature to the analytical signal.

Conflicts of interest

There are no conflicts to declare.

Table 5. Elemental concentrations (expressed as mean $\pm \frac{t s}{\sqrt{n}}$, 6 replicates) for fatty samples of different nature.

	UCO		HF		GA		CPO		PFAD	
	hTISIS (mg kg ⁻¹)	Cyclonic (mg kg ⁻¹)	hTISIS (mg kg ⁻¹)	Cyclonic (mg kg ⁻¹)	hTISIS (mg kg ⁻¹)	Cyclonic (mg kg ⁻¹)	hTISIS (mg kg ⁻¹)	Cyclonic (mg kg ⁻¹)	hTISIS (mg kg ⁻¹)	Cyclonic (mg kg ⁻¹)
Ba	3.0 ± 0.3	2.3 ± 0.8	1.11 ± 0.12	0.86 ± 0.03	< 0.024	< 0.17	< 0.024	< 0.17	< 0.024	< 0.17
Cd	< 0.176	< 0.6	0.63 ± 0.04	< 0.6	0.66 ± 0.13	2.1 ± 0.4	< 0.176	< 0.6	0.63 ± 0.11	< 0.6
Cr	0.046 ± 0.009	< 0.11	< 0.04	< 0.11	< 0.04	< 0.11	< 0.04	< 0.11	< 0.04	< 0.11
Cu	0.45 ± 0.07	< 0.11	0.69 ± 0.08	< 0.11	0.98 ± 0.05	0.49 ± 0.14	< 0.06	< 0.11	0.18 ± 0.06	< 0.11
Fe	28.0 ± 1.0	20.4 ± 1.1	2.33 ± 0.14	1.76 ± 0.10	3.9 ± 0.2	3.0 ± 0.2	2.5 ± 0.3	2.2 ± 0.2	< 0.06	< 0.22
Mg	2.5 ± 0.4	1.0 ± 0.3	0.9 ± 0.2	0.501 ± 0.06	5.9 ± 0.5	4.1 ± 1.0	1.5 ± 0.2	3 ± 2	< 0.011	< 0.042
Mn	0.042 ± 0.003	< 0.046	0.023 ± 0.014	< 0.046	0.27 ± 0.03	0.40 ± 0.07	0.09 ± 0.02	0.113 ± 0.013	0.149 ± 0.008	< 0.046
Si	6.5 ± 0.6	6.9 ± 0.5	6.0 ± 0.3	7.1 ± 0.5	6.9 ± 0.4	8.3 ± 0.7	7.5 ± 0.6	7.3 ± 0.6	4.4 ± 0.2	6.6 ± 0.5

Table 6. Elemental concentrations (expressed as mean $\pm \frac{t s}{\sqrt{n}}$, 6 replicates) for the different vegetable oil and fat samples.

	VO1 (mg kg ⁻¹)	VO2 (mg kg ⁻¹)	VO3 (mg kg ⁻¹)	VO4 (mg kg ⁻¹)	VO5 (mg kg ⁻¹)	VO6 (mg kg ⁻¹)	VO7 (mg kg ⁻¹)	VO8 (mg kg ⁻¹)	VO9 (mg kg ⁻¹)	VO10 (mg kg ⁻¹)	VO11 (mg kg ⁻¹)
Al	< 0.106	13.4 ± 1.6	1.2 ± 0.2	6.1 ± 0.6	0.70 ± 0.04	4.4 ± 0.3	1.1 ± 0.2	0.47 ± 0.09	1.1 ± 0.2	18.4 ± 1.9	1.6 ± 0.2
Ba	< 0.024	6.1 ± 0.9	2.0 ± 0.2	< 0.024	1.42 ± 0.12	0.95 ± 0.09	1.6 ± 0.3	< 0.024	0.81 ± 0.07	1.9 ± 0.3	4.3 ± 0.8
Ca	< 0.040	117 ± 3	17 ± 3	10.6 ± 1.6	7.8 ± 0.7	7.2 ± 0.9	7.2 ± 0.5	1.4 ± 0.6	6.8 ± 0.6	17 ± 4	3.9 ± 1.0
Cd	< 0.176	2.1 ± 0.5	0.35 ± 0.03	0.43 ± 0.04	0.38 ± 0.11	0.79 ± 0.07	2.01 ± 0.09	0.29 ± 0.14	0.61 ± 0.05	1.2 ± 0.2	0.80 ± 0.12
Cr	0.13 ± 0.02	1.02 ± 0.14	0.10 ± 0.02	0.15 ± 0.02	0.27 ± 0.02	0.24 ± 0.02	0.35 ± 0.03	0.11 ± 0.02	0.33 ± 0.02	0.46 ± 0.07	0.44 ± 0.07
Cu	< 0.062	1.7 ± 0.2	6.3 ± 0.3	0.61 ± 0.10	0.62 ± 0.07	0.99 ± 0.11	1.88 ± 0.09	< 0.062	2.5 ± 0.5	1.7 ± 0.3	1.35 ± 0.08
Fe	< 0.058	26.6 ± 1.6	0.28 ± 0.08	11.9 ± 1.3	1.68 ± 0.14	9.7 ± 0.5	7.4 ± 0.2	0.20 ± 0.05	0.58 ± 0.08	12.0 ± 1.5	5.7 ± 0.8
Mg	< 0.011	15.0 ± 0.5	1.29 ± 0.14	4.3 ± 0.6	0.59 ± 0.10	0.67 ± 0.08	0.85 ± 0.10	< 0.011	0.7 ± 0.4	5 ± 2	4.8 ± 0.4
Mn	< 0.013	34.6 ± 1.6	0.95 ± 0.07	< 0.013	0.09 ± 0.04	0.12 ± 0.04	0.26 ± 0.06	< 0.013	0.27 ± 0.06	0.16 ± 0.06	< 0.013
Mo	< 0.28	0.5 ± 0.3	< 0.28	< 0.28	< 0.28	< 0.28	0.73 ± 0.17	< 0.28	< 0.28	0.6 ± 0.2	2.2 ± 0.5
Ni	< 0.18	< 0.18	< 0.18	< 0.18	< 0.18	2.6 ± 1.6	< 0.18	< 0.18	< 0.18	< 0.18	2.0 ± 0.7
Pb	< 1.2	< 1.2	7.5 ± 1.3	1.65 ± 0.18	< 1.2	< 1.2	< 1.2	< 1.2	2.6 ± 0.4	< 1.2	3.8 ± 0.3
Si	2.6 ± 0.3	92 ± 6	6.0 ± 0.4	47 ± 6	5.76 ± 0.09	4.49 ± 0.12	5.5 ± 0.4	7.1 ± 0.2	6.4 ± 0.3	11.41 ± 0.03	26.4 ± 1.6
Ti	< 0.014	4.9 ± 0.8	0.20 ± 0.16	1.3 ± 0.2	0.56 ± 0.06	0.79 ± 0.09	1.11 ± 0.05	< 0.014	0.82 ± 0.02	1.23 ± 0.12	2.3 ± 0.5
V	< 0.054	1.3 ± 0.3	< 0.054	0.09 ± 0.04	0.74 ± 0.07	0.69 ± 0.04	1.2 ± 0.2	< 0.054	0.80 ± 0.07	1.1 ± 0.2	3.0 ± 0.6

Table 7. Elemental concentrations (mg kg⁻¹) in vegetable oils and fats found in the literature.

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Element	Palm oil ⁷	Crude Palm Oil ¹⁰	Palm Oil After Deodorization (POAD) ¹⁰	Crude Palm Oil ⁴⁵	POAD ⁴⁵	Suet oil ¹⁵	Cooking oils ⁴⁶
Cd	-	-	-	-	-	<LOD- 0.030	-
Cr	-	-	-	-	-	4.07-9.81	0.002-0.004
Cu	-	0.46±0.02	0.0297±0.0010	0.048	0.008	0.24-1.61	0.021-0.048
Fe	1.77-8.57	0.42±0.02	0.115±0.006	4.43	1.19	71.6-224	0.21-0.57
Mg	0.37-2.26	5.6±0.3	0.0207±0.0003	-	-	-	-
Mn	<LOQ-0.32	-	-	-	-	0.61-2.03	-

References

1 F.G. Lepri, E.S. Chaves, M.A. Vieira, A.S. Ribeiro, A.J. Curtius, L.C.C. De Oliveira, R.C. De Campos, *Appl. Spectrosc. Rev.*, 2011, **46**, 175–206.

2 B.S.F. Alves, F.I.M. Carvalho, A.S. Cruz, H.A. Dantas Filho, K.G.F. Dantas, *Rev. Virtual Quim.*, 2018, **10**, 542–550.

3 C. Duyck, N. Miekeley, C.L. Porto da Silveira, R.Q. Aucélio, R.C. Campos, G.P. Brandão, P. Grinberg, *Spectrochim. Acta Part B*, 2007, **62**, 939–951.

4 P.A. Mello, J.S.F. Pereira, M.F. Mesko, J.S. Barin, E.M.M. Flores, *Anal. Chim. Acta.*, 2012, **746**, 15–36.

5 F.A.C. Amorim, B. Welz, A.C.S. Costa, F.G. Lepri, M.G.R. Vale, S.L.C. Ferreira, *Talanta*, 2007, **72**, 349–359.

6 R. Sánchez, J. Lefevre, J.L. Todolí, *J. Anal. At. Spectrom.*, 2019, **34**, 664–673.

7 G.S. Valasques, A.M.P. DosSantos, D.G. DaSilva, J.P.S. Alves, M.A. Bezerra, *J. Braz. Chem. Soc.*, 2018, **29**, 2189–2196.

8 L. Yao, H. Liu, X. Wang, W. Xu, Y. Zhu, H. Wang, L. Pang, C. Lin, *Food Chem.*, 2018, **256**, 212–218.

9 D. Bakircioglu, Y.B. Kurtulus, S. Yurtsever, *Food Chem.*, 2013, **138**, 770–775.

10 A. Szydlowska-Czerniak, K. Trokowski, G. Karlovits, E. Szlyk, *J. Agric. Food Chem.*, 2013, **61**, 2276–2283.

11 A.L. Santos, R.M. Takeuchi, R.A.A. Muñoz, L. Angnes, N.R. Stradiotto, *Electroanalysis*, 2012, **24**, 1681–1691.

12 R. Sanchez, J.L. Todoli, C.P. Lienemann, J.M. Mermet, *J. Anal. At. Spectrom.*, 2012, **27**, 937–945.

13 Z. Ni, F. Tang, Y. Liu, D. Shen, R. Mo, *Anal. Lett.*, 2015, **48**, 1777–1786.

14 I. Juranovic, P. Breinhoelder, I. Steffan, *J. Anal. At. Spectrom.*, 2003, **18**, 54–58.

15 J. Jiang, L. Feng, J. Li, E. Sun, S.M. Ding, X. Bin Jia, *Molecules*, 2014, **19**, 4452–4465.

16 M.T. Lisboa, C.D. Clasen, D.C. De Sousa Vellar, E.Q. Oreste, T.D. Saint’Pierre, A.S. Ribeiro, M.A. Vieira, *J. Braz. Chem. Soc.*, 2014, **25**, 143–151.

17 F.H. Lyra, M.T.W.D. Carneiro, G.P. Brandão, H.M. Pessoa, E.V. de Castro, *Microchem. J.*, 2010, **96**, 180–185.

18 J.S. Almeida, G.L. Santos, G.C. Brandão, M.G.A. Korn, L.S.G. Teixeira, *Food Chem.*, 2019, **273**, 130–135.

19 E.C. Lourenço, E. Eyng, P.R.S. Bittencourt, F.A. Duarte, R.S. Picoloto, É.L.M. Flores, *Talanta*, 2019, **199**, 1–7.

20 Y.M. He, J.J. Chen, Y. Zhou, X.J. Wang, X.Y. Liu, *Anal. Methods*, 2014, **6**, 5105–5111.

21 J.R. De Souza, E.F. Dos Santos, C.B. Duyck, T.D. Saint’Pierre, *Spectrochim. Acta Part B*, 2011, **66**, 356–361.

22 <https://www.scpscience.com/>

23 J.R. De Souza, C.B. Duyck, T.C.O. Fonseca, T.D. Saint’Pierre, *J. Anal. At. Spectrom.*, 2012, **27**, 1280–1286.

24 E.J. Dos Santos, A.B. Herrmann, E.S. Chaves, W.W.D. Vechiatto, A.C. Schoemberger, V.L.A. Frescura, A.J. Curtius, *J. Anal. At. Spectrom.*, 2007, **22**, 1300–1303.

25 E.S. Chaves, M.T.C. DeLoos-Vollebregt, A.J. Curtius, F. Vanhaecke, *Spectrochim. Acta Part B*, 2011, **66**, 733–739.

26 R. Sañchez, J.L. Todolí, C.P. Lienemann, J.M. Mermet, *Spectrochim. Acta Part B*, 2013, **88**, 104–126.

27 R. Sánchez, J.L. Todolí, C.P. Lienemann, J.M. Mermet, *J. Anal. At. Spectrom.*, 2010, **25**, 178–185.

28 R. Sánchez, J.L. Todolí, C.P. Lienemann, J.M. Mermet, *J. Anal. At. Spectrom.*, 2010, **25**, 1888–1894.

29 C. Sánchez, C.P. Lienemann, J.L. Todolí, *Spectrochim. Acta Part B*, 2016, **115**, 16–22.

- 30 R. Sánchez, C. Sánchez, J.L. Todolí, C.P. Lienemann, J.M. Mermet, *J. Anal. At. Spectrom.*, 2014, **29**, 242–248.
- 31 C. Sánchez, C.P. Lienemann, J.L. Todolí, *Spectrochim. Acta Part B*, 2016, **124**, 99–108.
- 32 J.M. Craig and D. Beauchemin, *Analyst*, 1994, **119**, 1677–1682.
- 33 H. Wiltzsche, M. Winkler, P. Tirk, *J. Anal. At. Spectrom.*, 2015, **30**, 2223–2234.
- 34 A. Leclercq, A. Nonell, J.L. Todolí, C. Bresson, L. Vio, T. Vercouter, F. Chartier, *Anal. Chim. Acta*, 2015, **885**, 33–56.
- 35 A. Leclercq, A. Nonell, J.L. Todolí, C. Bresson, L. Vio, T. Vercouter, F. Chartier, *Anal. Chim. Acta*, 2015, **885**, 57–91.
- 36 J.M. Mermet, *Anal. Chim. Acta*, 1991, **250**, 85–94.
- 37 B.S. Whaley, K.R. Snable, R.F. Browner, *Anal. Chem.*, 1982, **54**, 162–165.
- 38 Y. Cheng, *Open J. Adv. Mater. Res.*, 2013, **641**, 346–350.
- 39 F. C. Pinheiro, A. I. Barros, J. A. Nóbrega, *Microchem. Journal*, 2019, **146**, 948–956.
- 40 F. C. Pinheiro, D. V. Babos, A. I. Barros, E. R. Pereira-Filho, J. A. Nóbrega, *J. Pharmaceut. Biomed.*, 2019, **174**, 471–478.
- 41 D.A. Sadler, F. Sun, S.E. Howe, D. Littlejohn, *Mikrochim. Acta*, 1997, **126**, 301–311.
- 42 R. Sánchez, J.L. Todolí, C.P. Lienemann, J.M. Mermet, *J. Anal. At. Spectrom.*, 2009, **24**, 391–401.
- 43 Z.-X. Ling, Y.-M. He, P.-Y. Wang, Y. Zhou, F. Ahmad, F.-F. Zhao, *Anal. Lett.*, 2016, **49**, 2461–2473.
- 44 M. das, G.A. Korn, D.S.S. dos Santos, B. Welz, M.G.R. Vale, A.P. Teixeira, D. de C.Lima, S.L.C. Ferreira, *Talanta*, 2007, **73**, 1–11.
- 45 M.I. Saleh, R.S. Murray, C.N. Chin, *J. Am. Oil Chem. Soc.*, 1988, **65**, 1767–1770.
- 46 A.M. Nash, T.L. Mounts, W.F. Kwolek, *J. Am. Oil Chem. Soc.*, 1983, **60**, 811–814.