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Preliminary Study on Characterization of Edible Oils Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Isotope Ratio Mass Spectrometry (IRMS)

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Abstract. *In recent years, increasing attention has been paid to oils consumed by humans. The human body uses oils in the diet for three purposes: energy source, structural component and powerful biological regulators. Elemental profiling of macro-, essential elements constitutes an important tool for quality control in terms of nutritional values of these products. Regarding this, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) determinations were performed to assess the quantitative complement of essential mineral and toxic metals content of different edible oil types, from Romania market, summing 33 samples, after microwave digestion. Additionally, the carbon stable isotope ratios ($\delta^{13}C$) were determined by Isotope Ratio Mass Spectrometry (IRMS) in order to differentiate the specific fingerprint of investigated oils.*

Keywords*: elements, ICP-MS, edible oil, carbon stable isotope ratio*

1. Introduction

Vegetable oils are widely used in food (edible oils), cosmetic, pharmaceutical and chemical industries. Regarding the world-wide food production, the edible oils derived from various plants and seeds, have an important role in human nutrition due to cholesterol reducing property [1, 2].

The quality of the edible oils, regarding their freshness and toxicity, can be evaluated through the determination of several trace metals, this being one of the most important criteria for the quality assessment of the oils from the health point of view [3-5]. The metals presence in edible oils is strongly influenced by the *i)* environmental conditions, *ii)* fertilizers and *iii)* production and storage processes [2, 6, 7]. Furthermore, the heavy metals traces affect the oxidation process of oils. For example, the elements such as Cu, Zn, Fe, Mn and Ni increase the rate of oil oxidation while other elements such as Cd, As and Pb are very important due to their toxicity and metabolic role, these representing a subject of food legislation. Taking into account the quality criteria, there were established the maximum permissible levels for As, Cu, Fe and Pb in olive oils [8], or for Cu and Fe in other edible oils [9].

The chemical analysis constitutes an important tool for the quality control in food industry where on-line, fast and simple methods are required [10-12]. Several studies have been carried out on the determinations of the metals in various edible oils, in different parts of the world, by using the analysis techniques, such as: flame and graphite furnace atomic absorption spectrometry [13, 14], neutron activation analysis [15], electrothermal atomic absorption spectrometry [16, 17], inductively coupled plasma-atomic emission spectrometry [18, 19] and inductively coupled plasma optical emission spectrometry [20].

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The elemental concentrations and the carbon isotope ratios of the edible oils can be used for the geographical discrimination and purity determination [21-24]. Taking into account the metabolic role of some metals, it is necessary an accurate elemental analysis of the edible oils, with high sensitivity and selectivity. Therefore, inductively coupled plasma mass spectrometry (ICP-MS) meets these requirements, being a trace-element detection tool with superior analytical capabilities [25, 26].

In this study, elemental concentrations and carbon isotope compositions in 33 edible oils samples were determined in order to evaluate their potential as parameters for food authentication.

2. Materials and methods

A number of 33 samples of edible vegetable oils from twelve different species (sunflower, olive, sesame, walnut, pumpkin, linen, hemp, maize, grape, colza, seabuckthorn and poppy), purchased from Romanian special shops, were analysed for their elements content (Mg, P, Ti, Cr, Mn, Fe, Co, Ni, Cu, Sr, Zr, Mo, Sn, Ba, Cd and Pb) and also it was investigated the $\delta^{13}C$ content in 11 types of these oils.

2.1. Elemental measurements

Generally, the sample preparation is a critical step for the determination of elements in food, in edible oils, respectively. Regarding this, there are presented different methods in the literature, which involve wet digestion, dry ashing, acid extraction or closed vessel-microwave [13, 27, 28]. For the chemical composition of the oils with large organic matter content, it is required the total digestion of the matrix in order to achieve a complete metal solubility.

The oil samples were subjected to microwave-assisted digestion by using nitric acid (69 %) and a closed iPrep vessels speed iwave system MARS6 (CEM One Touch Technology, USA). Thus, an amount of 0.3 g from each sample was digested in 10 ml nitric acid at high pressure and temperature. The programme used for digestion process is presented in Table 1.

Table 1. Digestion program for the metal extraction

Step	Power (psi)	Ramp Time (minutes)	Hold Time (minutes)	Temperature (°C)
Stage 1	1800	5	1	100
Stage 2	1800	7	10	150
Stage 3	-	10		Cooling

After 10 min of cooling, the liquid was transferred through a semi-automatic pipette into a 50 cm^3 volumetric flask of high-density polyethylene and it was filled with ultrapure water to the required volume.

Deionized ultrapure water (18 $M\Omega \cdot cm^{-1}$), produced by a Milli-Q integral water purification system (EMD Millipore Corporation, Billerica, MA, U.S.A) and ultra-pure nitric acid (HNO_3) were used. Therefore, the vessels and the tools used for sampling and samples treatment were cleaned with 10 % (v/v) nitric acid and deionized water.

Calibration standard solutions were prepared by successive dilution of *i)* high purity ICP-multielement calibration standard (10 $\mu g \cdot L^{-1}$ from twenty-nine elements ICP-MS standard, 5% HNO_3 matrix, ICP Multi-Element Standard Solution XXI CertiPUR®, Merck KGaA Frankfurter, Darmstadt, Germany) and *ii)* high purity ICP monoelement calibration standard (10 $\mu g \cdot mL^{-1}$ from Hg, 5% HNO_3 matrix, CertiPUR®, Merck KGaA Frankfurter, Darmstadt, Germany). Also, an internal standard (Analytik Jena, Germany) was prepared through dilution of 100 $\mu g \cdot mL^{-1}$ solution containing Li, Tb, Y, Sc, Bi, In in 2% HNO_3 matrix.

The element concentrations were measured with an inductively coupled plasma quadrupole mass spectrometer ELAN DRC-e, (Perkin Elmer, United Kingdom). The operating conditions were optimized by using a tuning solution that contains 10 $\mu g \cdot L^{-1}$ Ba, Cd, Ce, Cu, In, Mg, Pb, Rh, U, (Elan 6100 Setup/Stab/Masscal Solution, Perkin Elmer, United Kingdom). All measurements were performed two times, with ten replicates.

The performances of the ICP-MS are depended by the operating conditions which are presented in table 2.

Table 2. ICP-Q-MS operating conditions

Parameter	Value
Nebulizer gas flow rate	0.92 $Lmin^{-1}$
Auxiliary gas flow	1.2 $Lmin^{-1}$
Plasma gas flow	15 $Lmin^{-1}$
Lens voltage	7.25 V
Inductively coupled plasma radio frequency power (ICP RF Power)	1100 W
CeO/Ce	0.031
Ba^{++}/Ba^{+}	0.016

Dynamic reaction cell technology (DRC) was used to minimize interferences by placing a pressurized closed cell between the ion lens and the quadrupole mass analyser (QMS) in the ICP-MS. The plasma parameters were chosen to obtain a good compromise between high sensitivity and low oxide levels.

2.2. Stable isotope measurements

In order to determine the isotope fingerprint, it was converted the carbon from oil to carbon dioxide (CO_2). The conversion of organic carbon to CO_2 was made by dry combustion (550 °C) under oxygen excess. Further, the CO_2 was separated from the other combustion gases by cryogenic distillation. The analyses were performed by using an isotope ratio mass spectrometer (IRMS, Delta V Advantage, Thermo Fisher Scientific, Ma, U.S.A) coupled with a dual inlet system.

The variations of stable isotope ratios were reported as parts per thousand (‰) deviation by using equation (1):

$$\delta\ (‰) = (R_{sample}/R_{standard}) - 1 \qquad (1)$$

where:

R - heavy and light isotopes ratio;

R_{sample} – sample isotope ratio;

$R_{standard}$ – standard isotope ratio.

Each sample was analysed in duplicate and the average was reported. NBS 22 (oil) was used as reference material and the uncertainty limit for $\delta^{13}C$ was ± 0.2 ‰.

3. Results and discussions

The chemical and isotope compositions depend on both the ecology of where the product was grown and the processes involved during preparation.

3.1. Element composition of edible oils

In Figure 1, Figure 2 and Figure 3 are presented the distribution of elements contents in the studied oils.

Elements, such as Mn, Co, Cr, Fe, Cu, Ni, Pb and Cd have adverse effect on the oxidative stability of edible oils [29]. Cu and Fe catalyse the decomposition of hydroperoxides and lead to faster formation of undesirable substances. Micronutrients, namely Cu, Cr, Mn and Fe, are essential for plant growth and are also required in human diet, but in reasonable quantities, because in high doses these are toxic.

From the results illustrated in Figure 1, it can be noticed that the highest contents of Cr and Fe were found in maize samples, 2.4 mg·kg^{-1} and 3.8 mg·kg^{-1}, respectively, followed by the sesame samples, with 1.5 mg·kg^{-1} and 2.0 mg·kg^{-1}, respectively. Also, there were found high contents of Cr in colza and linen samples, 1.9 mg·kg^{-1} and 1.6 mg·kg^{-1}, respectively.

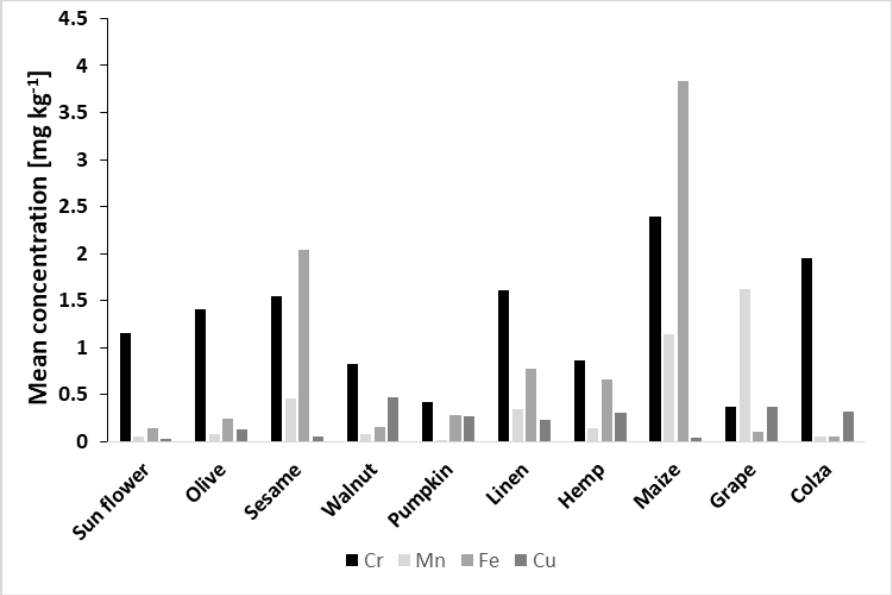

Figure 1. The mean Cr, Mn, Fe and Cu contents in oils

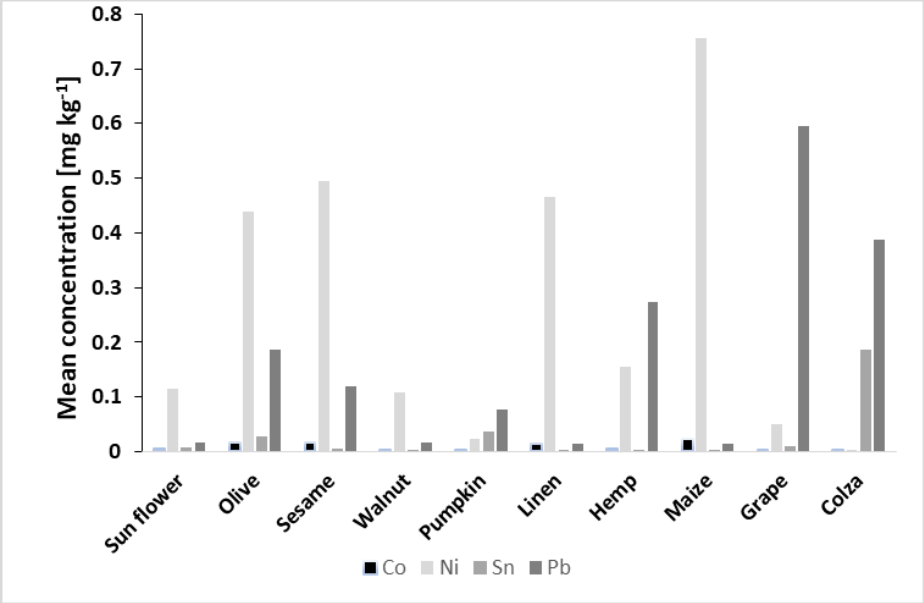

Figure 2. The mean Co, Ni, Sn and Pb contents in oils

At the opposite, the micronutrients found in low concentrations levels in almost all samples were Cu and Mn and their lowest concentrations were in sun flower oil, 0.026 mg·kg^{-1} and 0.049 mg·kg^{-1}, respectively, these values being lower than data reported in literature [2].

The mean content of Cu in olive oils was about 0.130 mg·kg^{-1}, this being in accordance with values reported in different studies [29-33]. Also, the Fe concentration in olive oil, 0.240 mg·kg^{-1}, was below the limit established by the IOC, namely 3.0 mg·kg^{-1} [34].

Regarding the Ni concentration, the highest value was found in maize oil, namely 0.756 mg·kg^{-1}, followed by sesame, linen and olive oils, with 0.495 mg·kg^{-1}, 0.466 mg·kg^{-1} and 0.438 mg·kg^{-1},

respectively. The second main element, revealed from Figure 2, was Pb. The highest Pb concentration was found in grape oil, namely 0.596 mg·kg^{-1}, followed by colza, hemp and olive oils, with 0.387 mg·kg^{-1}, 0.273 mg·kg^{-1} and 0.187 mg·kg^{-1}, respectively.

As it can be seen from Figure 3, the macroelement with the highest concentration in edible oil samples is P. Its concentration was between 14.230 mg·kg^{-1} (in sea buckthorn) and 27.057 mg·kg^{-1} (in grape).

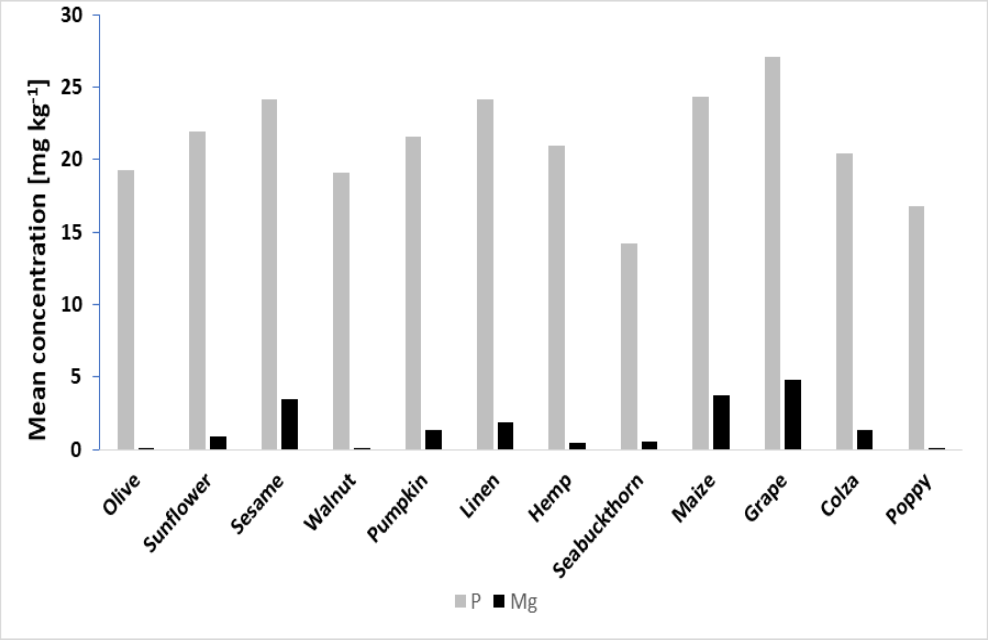

Figure 3. The mean P and Mg contents in oils

Regarding the contents of Mg in edible oils, these are almost unnoticeable for olive, walnut and poppy samples, the values being below 0.120 mg·kg^{-1}. This element was found in high concentration in grape, sesame and maize: 4.774 mg·kg^{-1}, 3.754 mg·kg^{-1}and 3.476 mg·kg^{-1}, respectively.

The total P content gives informations related to the refining process and consequently is useful for process optimization. P is found in most crude vegetable oils, having an important influence on the final oil quality and being an indicator of phospholipid removal [35-37].

3.1. Stable isotope composition of edible oils

Regarding the isotope composition of edible oils from this study, the lowest $\delta^{13}C$ mean value was obtained for linen oils, -32 ‰, whereas the highest mean value was recorded for walnut, -26.3 ‰. For olive oil samples, the $\delta^{13}C$ values were between -30.6 ‰ and -28.3 ‰, the higher values being for the samples originated from Greece, reflecting the geo-climatic dependence of this parameter. These values are in accordance with data found in literature [38].

It was also observed that the production process could influence the isotope composition. Thus, the $\delta^{13}C$ mean values obtained for cold pressed sunflower oil and for refined sunflower oil were -31.1 ‰ and -29.6 ‰, respectively.

Colza and poppy oils have the same value; therefore, the samples could not be distinguished.

For sesame oil samples, the values were different from country to country, ranging from -28.4 ‰ for an ecological extra virgin sesame oil from Germany to -30.1 ‰ for a cold pressed sesame oil from Romania.

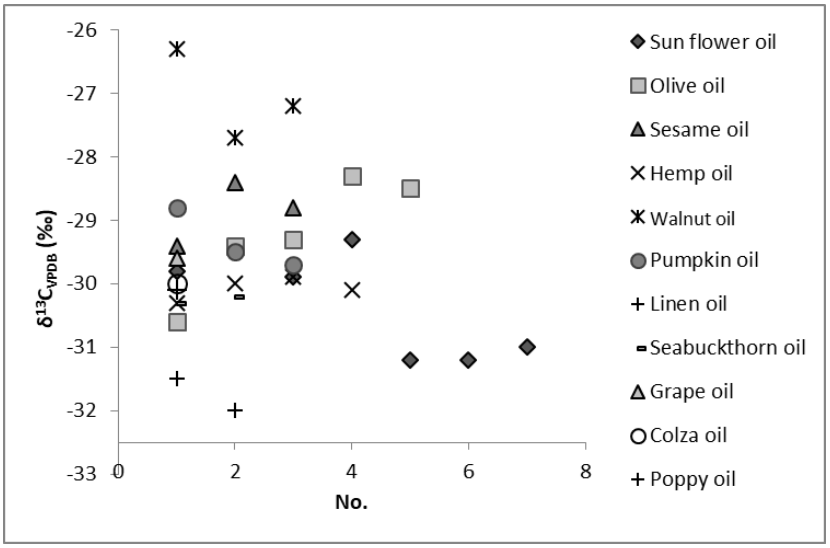

Figure 4. Isotopic fingerprint of studied oil samples

4. Conclusions

The micro and macro elements were determined in different edible oil samples from various plant growth areas in order to establish their quality. The upper control limits have not been exceeded. Also, it was demonstrated that the carbon isotope ratio analysis is a powerful tool to prevent the oil adulteration.

Furthermore, it was remarked both that the olive oil samples from different growth areas and the various processes used to obtain the sunflower oils can be separated based on their $\delta^{13}C$ contents.

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