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ELEMENTAL CONTENT OF EDIBLE OILS STUDIED BY NEUTRON ACTIVATION ANALYSIS

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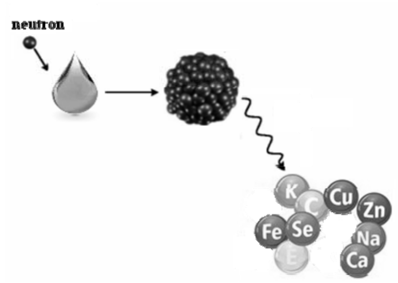
Assessment of the elemental content of edible oils is important from toxicological and nutritional viewpoints. Neutron activation analysis was used to determine the chemical content of virgin sunflower oil, two types of refined sunflower oils commercially available in Romania, and virgin olive oil produced in Algeria. A total of 17 elements: Na, Al, Cl, K, Ca, Ti, V, Mn, Co, Zn, Cu, As, Br, Sr, Sb, I, and W were determined in the studied oils. In all samples the concentrations of K, Ti, V, Co, Cu, As, Sr, and I were below the detection limit of their determination. The highest concentration of Br was detected in the olive oil sample. The concentrations of heavy metals were found to be below the permissible limits for edible oils.



INTRODUCTION

Edible oils are widely used for cooking and alimentary, cosmetic, pharmaceutical and chemical applications.[1] The human body uses oils and fats in the diet as an energy source and as a structural component.[2,3] In particular, the vegetable oils are beneficial and popular due to their cholesterol-lowering effect.[3]

Olive oil consists of triglycerides, with a high content of mono-unsaturated fatty acid, whereas seed oils are rich in polyunsaturated linoleic acid.[4,5] However, for the quality of edible oils, not only the organic composition, but also the presence of inorganic species is important.[6]

The relevance of the elemental content is due to the metabolic role of some elements in the human organism.[7] Moreover, the inorganic profile was related to some quality indicators of oils such as the freshness or their specific benefits on human nutrition and health.[8] The presence of metal traces can be due to soil chemical composition or to different human activities, such as the use of fertilizers and pesticides, the pollution due to industry or transport.[1,2,5,8] The major source of heavy metals in vegetal oils and greases is also the metallic parts of the processing equipment and the hydrogenation catalysts.[1,2,5,9]

Information regarding the admissible levels of metals and other toxic elements in oil is limited and exists just for some metals. The European Community sets limit only for Pb in edible oils, which is 0.1 mg/kg. [10] The limit for copper in virgin and refined olive oil established by the

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International Olive Council is 0.4 mg/kg and 0.1 mg/kg, respectively.[11] The maximum permissible concentration of arsenic in vegetable oils is 0.1 mg/kg.[12]

The most common techniques used for metal determination in oils are atomic absorption spectrometry, [2,8,9] inductively coupled plasma optical emission spectrometry,[13] ion chromatography,[6] inductively coupled plasma-atomic emission spectrometry,[7] and inductively coupled plasma mass spectrometry.[14]

However, the above mentioned methods have some disadvantages, among of which are the need of organometallic standards for calibration, the use of dangerous organic solvents or sample digestion procedures using concentrate acid or acid mixtures.[8]

Neutron activation analysis (NAA) is considered an interesting tool due to its high sensitivity, simultaneous quantitative multi-element determination, nondestructive character and minimization of the time required for samples preparation.

In the present study elemental content of several sunflower oils available on the Roumanian market, and virgin olive oil produced in Algeria was determined by NAA. This study is a continuation of the work performed by N. Balasa *et al.*[15] on chemiluminescence from these materials.

RESULTS AND DISCUSSION

The average concentrations of the elements determined by NAA in comparison with the elements determined by other techniques are presented in Table 1.

The quality of edible oils is directly related to the concentration of trace metals in such samples. Trace levels of metals such as Fe, Cu, Ca, Mg, Co, Ni and Mn are known to increase the oil oxidation rate, affecting the quality of these products, while other elements such as Cr, Cd, and Pb must be strictly controlled due to their toxicity.[2,16]

The concentration of Na, Al, Cl, Mn, Br, and Sb were below the detection limits for all studied samples. The value of Ca content was below the detection limit only for virgin sunflower oil (VF), and Zn for refined sunflower oil RF1 and virgin olive oil (VO). The concentration of K, Ti, V, Co, Cu, As, Sr, and I, were below the detection limits in the given experimental conditions.

The concentration of Na was nearly 2 times higher in the sunflower oil RF1 than in the other oil samples. The concentrations were higher than the data presented in reference, [2] but lower than the data reported by Cindric *et al.* [7] The concentrations of Al and Cl varied from 3.7 μg/g and 16 μg/g in the virgin sunflower oil to 12 μg/g and 31 μg/g for the sunflower oil RF1, respectively.

The concentration of Ca for virgin sunflower oil was 17 μg/g, but for the refined oil it was below the NAA detection limit. Manganese was detected in all oil samples with concentration ranging from 0.06-0.12 μg/g. These data are in a good agreement with those obtained by Mendil *et al.* [2]

Antimony was detected in all samples in the concentration range of 0.05−0.2 μg/g. Zinc was determined in the olive oil, sunflower oil RF1, and tungsten in the virgin sunflower oil and in the olive oil.

The concentration of Br in the examined samples ranges from 0.7 to 84 μg/g except for the olive oil showing the highest Br concentration.

It is considered that copper and iron are potential contaminants of the oil derived from the processing equipment. [16] In the present study Fe was not detected in any of the oil samples, and Cu concentration was below the detection limit. Al detected in all oil samples most probably comes from crucibles in which thermooxidation takes place.

The high content of Br, W, and Zn in the virgin olive oil in comparison with the sunflower oils can be associated with the geographical features of the region (soil type, pesticides, etc.), where olives were grown, processing and storage conditions. In the same way the differences in the metal concentrations in the sunflower oil samples can be explained.

MATERIALS AND METHODS

Materials

Four types of oil were used: virgin sunflower oil (VF), refined sunflower oils RF1 and RF2, and virgin olive oil (VO). Oil samples were subjected to thermooxidation in an oven with air circulation at the temperature of 130 °C. The thickness of the obtained oil layer was around 5 mm. For NAA samples were cut into small pieces. The sample weight was around 250 mg in each case. Each sample was analyzed in triplicate.

Table 1

Concentration of elements (μg/g) in studied edible oil samples as compared to other literature data

Element	NAA (present data) μg/g				NAA [5]		FAAS [2]		ICP-AES [7]	
	Virgin sunflower oil (VF)	Virgin olive oil (VO)	Sunflower oil RF1	Sunflower oil RF2	Sunflower oil	Olive oil	Sunflower oil	Olive oil	Sunflower oil	Olive oil
Na	14±3	20±6	27±7	11±2.4	4.6	12.9	1.8±0.1	8.7±0.8	24.7	34
Al	3.7±0.2	5.2±0.4	12±0.5	7±0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cl	16±4.8	20±6	31±9.3	24±8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
K	<21	<20	<24	<22	5.9	47.2	2.5±0.2	2.1±0.2	<0.3	<0.3
Ca	17±5	<26	<23	<17	n.d.	n.d.	174±17	76±7.5	0.5	2.0
Ti	<4.5	<12	<2.1	<1.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
V	<0.006	<0.02	<0.01	<0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	0.09±0.02	0.21±0.04	0.12±0.03	0.06±0.01	n.d. 0	n.d.	0.12±0.01	0.04±0.004	n.d.	n.d.
Fe	n.d.	n.d.	n.d.	n.d.	7.2	4.5	105±10	139±10	15	15.5
Co	<0.07	<0.05	<0.26	<0.17	0.041	0.016	0.5±0.05	1.3±0.1	n.d.	n.d.
Zn	<1.2	2.3±0.5	3.5±1	<2.6	0.8	0.6	1.1±0.1	1.03±0.1	3.1	3.4
Cu	<0.4	<1.2	<0.6	<0.7	n.d.	n.d.	0.1±0.01	0.7±0.06	n.d.	n.d.
As	<0.02	<0.2	<0.03	<0.02	<0.1	<0.09	n.d.	n.d.	n.d.	n.d.
Br	0.7±0.2	84±21	0.8±0.2	0.7±0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sr	<2.3	<3.7	<3.8	<4.3	<1.8	<4.1	n.d.	n.d.	n.d.	n.d.
Sb	0.05±0.01	0.1±0.02	0.2±0.03	0.1±0.03	<15	<14	n.d.	n.d.	n.d.	n.d.
I	<0.04	<0.2	<0.07	<0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
W	0.7±0.1	2.5±0.6	<1.7	<0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 2

Comparison of the passport data and concentrations obtained experimentally by the NAA for used reference materials

Reference material	Elements							
	1633b		2709		1633c		433	
	Certified value, µg/g	Experimental Value, µg/g	Certified value, µg/g	Experimental Value, µg/g	Certified value, µg/g	Experimental Value, µg/g	Certified value, µg/g	Experimental Value, µg/g
Na	2100	1900	11600	11600	1710	1710	13500	10700
Al	15100	15100	75000	79400				
K	19500	18100	20300	18500	17700	17700	16600	18800
Ca	15100	15600	18900	19900				
Ti	7910	7910	3420	4320				
V	296	296	112	108				
Mn	132	132	538	534				
Co					43	43	21.9	14.8
Zn					235	235	101	102
As					186	186	18.9	19.4
Br							67	67
Sb					8.5	8.6	1.9	1.9
Sr					901	900	302	304
I			5	6.8				

Methods

Elemental content of the samples was determined after their irradiation at the radioanalytical complex REGATA at the pulsed reactor IBR-2. IBR-2 provides activation with thermal, epithermal and fast neutrons. Thermal NAA takes advantage of the high intensity of neutrons available from the thermalization of fission neutrons and the large thermal neutron cross sections for most isotopes. Epithermal is taken to be neutrons with energies from the Cd «cut-off» of 0.55 eV up to approximately 1 MeV. In general, the activation cross sections of the matrix elements of environmental samples are inversely proportional to the neutron energy (1/*v* low).[17]

To determine short-lived isotopes Mg, Al, Cl, K, Ca, Ti, V, Mn, Cu and I, the conventional (full neutron spectrum) irradiation channel was used. The samples were irradiated for 10 min under a thermal neutron fluency rate of approximately 1.6×10^{13} n cm^{-2} s^{-1} and measured after 5 min and 12 min of decay for 3 min and 9–10 min, respectively.

To determine long-lived isotopes, namely, Na, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Rb,Sr, Zr, Mo, Sb,Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Hf, Ta, W, Th, and U, the cadmium screened channel (epithermal and fast neutrons) under a resonance neutron fluency rate of approximately 3.31×10^{12} n cm^{-2} s^{-1} was used. The samples were irradiated for 120 hours, repacked and measured using high purity germanium detectors twice, after 3 and 16 days of decay. Measurement times were 45 min and 150 min, respectively.

The range of half-lives for short lived isotopes varies from 2 to 10 min and for long-lived ones from 10 hours to several years.

The quality was assured by the use of the certified reference materials: The correlation between the certified (recommended) values of concentrations and the experimental ones is presented in Table 2.

The validation of data obtained by NAA is proved by inter-laboratory studies like Wageningen evaluating programs for analytical laboratories (WEPAL) for different type of samples.[18,19]

CONCLUSIONS

Neutron activation analysis can be efficiently applied for determination of elemental content of different types of edible oils. The obtained results indicate differences in the metal concentrations of edible oils.

The concentration of K and Cl in the sunflower oil RF1 differs considerably from the other oils. The virgin olive oil samples contain high amounts of Br, W and Zn and virgin sunflower oil − higher Ca amount in comparison to the other oil types. The results obtained are in good agreement with the data of other investigations.

The concentrations of heavy metals in the studied oils do not exceed the recommended legal limits established by the World Health Organization for human consumption.[20]

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