## Determination of some inorganic metals in edible vegetable oils by inductively coupled plasma atomic emission spectroscopy (ICP-AES)

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#### RESUMEN

Determinación de algunos metales inorgánicos en aceites vegetales comestibles mediante espectroscopía de emisión atómicacon fuente de plasma acoplado inductivamente (ICP-AES).

En este estudio se analizó espectrométricamente el contenido en metales (Cu, Fe, Mn, Co, Cr, Pb, Cd, Ni, and Zn) de 17 aceites vegetales comestibles mediante ICP-AES. Las concentaciones más elevadas se encontraron para el cobre en el aceite de almendra (0.0850 mg/kg), para el hierro en el aceite de maiz(c),(0.0352 mg/kg), para el manganeso en el aceite de soja (0.0220 mg/kg), para el cobalto en el aceite de girasol (b) (0.0040 mg/kg), para el cromo en el aceite de almendra (0.0010 mg/kg), para el plomo en el aceite de oliva virgen (0.0074 mg/kg), para el cadmio en el aceite de girasol (e) (0.0045 mg/kg), para el niquel en el aceite de almendra (0.0254 mg/kg) y para el zincen el aceite de almendra (0.2870 mg/kg). Los metales se extrajeron a partir de bajas cantidades de aceite (2-3 g), con una solución de ácido nítrico al 10%. Se discute el método y se conclluye que el método propuesto es simple y permite la determinación en aceites vegetales comestibles con una precisión estimada inferior al 10% para Cu, 5% para Fe, 15% para Mn. 8% para Co, 20% para Pb, 5% para Cd, 16% para Ni y 11% para Zn.

PALABRAS CLAVE: Aceite comestible – Aceite vegetal – ICP-AES – Metales tóxicos.

#### SUMMARY

# Determination of some inorganic metals in edible vegetable oils by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Seventeen edible vegetable oils were analyzed spectrometrically for their metal (Cu, Fe, Mn, Co, Cr, Pb, Cd, Ni, and Zn) contents. Toxic metals in edible vegetable oils were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The highest metal concentrations were measured as 0.0850, 0.0352, 0.0220, 0.0040, 0.0010, 0.0074, 0.0045, 0.0254 and 0.2870 mg/kg for copper in almond oil, for iron in corn oil-(c), for manganese in soybean oil, for cobalt in sunflower oil-(b) and almond oil, for chromium in almond oil, for nickel almond oil and for zinc in almond oil respectively. The method for

determining toxic metals in edible vegetable oils by using ICP-AES is discussed. The metals were extracted from low quantities of oil (2-3 g) with a 10% nitric acid solution. The extracted metal in acid solution can be injected into the ICP-AES. The proposed method is simple and allows the metals to be determined in edible vegetable oils with a precision estimated below 10% relative standard deviation (RSD) for Cu, 5% for Fe, 15% for Mn, 8% for Co, 10% for Cr, 20% for Pb, 5% for Cd, 16% for Ni and 11% for Zn.

KEY-WORDS: Edible oil – ICP-AES – Vegetable oils – Toxic metals.

## 1. INTRODUCTION

Vegetable oils are widely used in the cooking and food processing, cosmetics, pharmaceutical and chemical industries (Dugo et al., 2004). Plants and animals depend on some metals as micronutrients. Metal elements such as Na, K, Ca, Mg, Fe, Cu, Zn and Mn, are essential nutrients for human growth. However, certain forms of some metals can also be toxic, even in relatively small amounts, and therefore pose a risk to the health of animals and people. Metal elements such as Cd, Pb, Cd, Co, and Cu, could also have detrimental effects on health. While the effects of chronic exposure to trace amounts of some metals are not well understood, many incidents tells us about the seriousness of high levels of exposure to some toxic metals, especially cadmium, chromium, cobalt, nickel and lead (Buldini, Ferri, & Sharma, 1997; Demirbas, 2001; Garrido et al., 1994).

The harmful effects induced by toxic metal only occur when they are overdosed. In general, a hazardous metal is defined as a metal which could induce adverse symptoms in the human body when consumed even in trace amounts. There is currently considerable interest in the determination of heavy metals in foods. It is necessary to study the migration of trace elements and to monitor the highly toxic microcomponent content at all stages of the ecological chain (soils, waters, biological

systems) because there are immediate sources of heavy metals that reach the human organism (Kubrakova et al., 1994). It is known that some living organisms possess the ability to take in and accumulate certain elements in their structures, especially metals, at high concentrations. The presence of trace metals is an important factor as far as the quality of edible oil is concerned. The presence of heavy metals in edible oils is due to both endogenous factors, connected with the plant metabolism, and hexogenous factors due to contamination during the agronomic techniques of production and the collection of olives and seeds during the oil extraction and treatment processes, as well as systems and materials of packaging and storage (Coco et al., 2003; Dantas et al., 2003). The presence of metals in vegetable oils depends on many factors: they might originate from the soil, fertilizers, or presence in the industry or highways near the plantations, and be incorporated into the oil (La Pera et al.2002a). Sample preparation is a critical step in the analytical procedure for the determination of heavy metals in vegetable oils; classical methods usually employed are wet digestion, dry ashing, acid extraction, closed vessel and focused open-vessel microwave dissolution and dilution (Allen et al., 1998; Garrido et al., 1994). The determination of these metals in the vegetable oils requires specific analytical procedures such as emission and atomic absorption spectrophotometric techniques as well as electroanalytical techniques. (Hendrikse et al., 1991; Coco et al., 2003; Buldinia et al., 1997; Zeiner et al., 2005; Cindric et al., 2007).

Trace levels of metal ions (Cu, Fe, Mn, Co, Cr, Pb, Cd, Ni, and Zn) are known to have adverse effect on the oxidative stability of edible oils. Transition metals such as copper and iron catalyze the decomposition of hydroperoxides and lead to more rapid formation of undesirable substances. Taking into account the metabolic role of some toxic metals, the development of fast and accurate analytical methods for trace element determination in edible vegetable oils is important from the viewpoint of both production quality control and food analysis. The content of metals and their chemical forms in edible oils depend on several factors. The metals might originate from the soil and fertilizers and be intimately incorporated into the oil. They might be introduced during the production process (by processing actions such as bleaching, hardening, refining and deodorization) or by contamination from the metal processing equipment and thus be suspended in the oil (Leonardis, Macciola, & Felice, 2000).

In this paper we report an investigation on the feasibility of the direct extraction of toxic metals from vegetable oils using a dilute nitric acid solution before ICP-AES. The application of a direct spectrometric technique, particularly ICP-AES, is the best way to effect such a difficult analysis. These methods suffer disadvantages such as the possible loss of volatile metal species during ashing, contamination in the course of the digestion or chelation process, or non quantitative recoveries especially when numerous extraction steps are involved (Karadjova *et al.*, 1998).

## 2. MATERIALS AND METHODS

## 2.1. Materials and Containers

All reagents and standard stock solutions used were from Merck. The concentrated nitric acid  $(HNO_3)$  was pure, specific for trace analysis, and was diluted to 10 % (v/v) concentration with deionized water. All containers, including test tubes with stoppers, were in polypropylene and were cleaned with 5% (v/v) hydrochloric acid and the deionized water. The blank consisted of the 10% dilute nitric acid and deionized water.

## 2.2. Analysis

In this study, 17 samples of edible vegetable oils, corresponding to six different species, were used for their metal content. The oil samples were taken from some food supply markets in Turkey. Oil samples include soybean-, hazelnut-, almond-, natural olive-, riviera olive-, virgin olive-, olive (frying)-, sunflower- and corn- oil. Metal ion concentrations were determined as three replicates by Varian Vista ICP-AES. A calibration curve was obtained to see the linear relationship between absorbance and metal concentration in the concentration range being used .

## 2.3. Preparation of standards

The first standard stock solutions had a 1.0 mg/L concentration of each metal and these were used for the preparation of aqueous standard solutions after appropriate dilution with 10 % nitric acid. The concentration ranges of the working solutions were 0.001- 0.1 ppm for all metals. The procedure of the spiked standard preparation was the following: 1 ml of 10% nitric acid containing different concentrations of metal (10-50 ppb) was added to 1g of oil samples. The extraction was performed as described for the preparation of sample section.

## 2.4. Quality control

To assure the accuracy of the data reported, recovery experiments were performed. A certain amount of each element of interest depending on its expected concentration in the sample was added prior to the mineralization of oil samples. The experiments were performed in triplicate. To avoid contamination of the specimens, all steps in the sample preparation procedure were carried out in a laboratory equipped for trace element analysis. Reagent blanks were prepared and measured in the same way as the samples.

#### 2.5. Preparation of samples

The types of oil samples analyzed were soybean-, hazelnut-, almond-, natural olive-, riviera olive-, virgin olive-, olive (frying)-, sunflower- and corn-oil. An aliquot (2.0-3.0 g) of every oil was weighed directly into the test tube and 1 ml of the 10% dilute nitric acid was added. The oil-acid mixture was shaken at 50 Hz for 60 s with a test tube mixer until the layers were completely mixed. The capped test tube was placed in a shaking water bath at 50°C for 2 h. After centrifugation at 2800 rpm for 10 min, the lower acid aqueous layer was withdrawn with a pipette and was filled to 25 ml by adding deionized water and then loaded directly into the auto sampler of the ICP-AES (Leonardis, Macciola, & Felice 2000). Then, measurements were carried out at 396.152 (Al), 228.802 (Cd), 324.754 (Cu), 259.940 (Fe), 257.610 (Mn), 238.892 (Co), 257.716 (Cr), 220.353 (Pb), 231.604 (Ni) and 213.857 (Zn) waves.

#### Working conditions of ICP-AES:

Instrument: ICP-AES (Varian-Vista RF Power: 0,7-1,5 kw (1,2-1,3 kw for Axial) Plasma gas flow rate (Ar): 10,5-15 L/min. (radial) 15 L/min (axial) Auzilary gas flow rate (Ar): 1,5 L/min Viewing height: 5-12 mm Copy and reading time: 1-5 s (max.60 s) Copy time: 3 s (max. 100 s)

## 2.6. Statistical Analyses

Results of the research were analyzed for statistical significance by analyses of variance (Püskülcü and Ikiz 1989). Standard deviations were calculated for each oil and are based on measurements in triplicate.

## 3. RESULTS AND DISCUSSION

The most commonly used techniques for the determination of metals in oil samples are ICP-AES. Because edible vegetable oil or fat standards for inorganic species do not exist, the detection of copper, iron, manganese, cobalt, chromium, lead, cadmium, nickel and zinc metals have been determined by ICP-AES technique. They were extracted by treating commercial edible oils with diluted nitric acid. Results are presented as the mean of the mean values of each oil and standard deviations were calculated for each oil and are based on measurements in triplicate.

In Table 1 the average quantities of metal (ppb) recovered in two trials with regards to the additional standards are given for the experimental section. The accuracy of the results, estimated in a percent average of the standard addition recoveries, was higher than 95% for all metal ions. When the concentration of metal ion was very low, the results

Table 1
Averages of the standard addition recoveries
obtained by two independent determinations

Metal	ppb added	ppb found
Cu	10 20	9 ± 2 17 ± 3
Fe	20 40	18 ± 3 37 ± 5
Mn	20 30	18 ± 2 28 ± 3
Со	5 10	4 ± 1 9 ± 2
Cr	5 10	4 ± 2 8 ± 2
Pb	5 10	4 ± 2 8 ± 3
Cd	5 10	4 ± 1 9 ± 2
Ni	5 10	4 ± 1 8 ± 3
Zn	40 50	$\begin{array}{c} 37 \pm 4 \\ 46 \pm 6 \end{array}$

obtained were influenced by noise and instrumental interference.

The average amount toxic metals in 17 selected samples of edible vegetable oil supplied from different markets are given in Tables 2, 3 and 4. In this study, the highest metal concentrations were measured as 0.0850, 0.0352, 0.0220, 0.0040, 0.0010, 0.0074, 0.0045, 0.0254 and 0.2870 mg/kg for copper in almond oil, for iron in corn oil-(c), for manganese in soybean oil, for cobalt in sunflower oil-(b) and almond oil, for chromium in almond oil, for lead in virgin olive oil, for cadmium in sunflower oil-(e), for nickel almond oil and for zinc in almond oil respectively. The lowest copper contents found were 0.0082, for corn oil-(c); iron, 0.0039 for corn oil-(a); manganese, 0.0007, for riviera olive oil-(a); cobalt, 0.0001 for sunflower oil-(a); chromium, 0.0005 for sunflower oil-(d); lead, 0.012 for sunflower oil-(c); cadmium, 0.0003 for almond oil; nickel, 0.0013 for riviera olive oil-(c) and zinc, 0.0184 mg/kg for sun flower oil-(e). La Pera et al. (2002a, 2002b) determined the trace element composition of a large number of Italian olive oil samples in concentrations ranging from 0-2.1 µg/kg for Cd, 9.1 -50.0 µg/kg for Cu, 15.4-70 µg/kg for Pb and 68.0 -576.0 µg/kg for Zn, although little data was found about the presence of these elements in seed oils (Nash et al.1983; Martin-Polvillo et al.,1994). The values reported were 1.0-5.5 µg/kg for Cd, 3.1-129.0 µg/kg for Cu, and 3.6-152.0 µg/kg for Pb, and no information was found on zinc. The European Community fixed the legal limits for lead concentration in vegetable oils at 100 µg/kg (CE

Edible Oils	Cu	Fe	Mn
Soybean oil	0,0273* ± 0,0005**	0,0129 ± 0,0004	0,0220 ± 0,0011
Hazelnut oil	0,0146 ± 0,0006	$0,0054 \pm 0,0003$	0,0195 ± 0,0010
Almond oil	$0,0850 \pm 0,0012$	$0,0216 \pm 0,0008$	0,0175 ± 0,0009
Natural olive oil	0,0174 ± 0,0002	0,0178 ± 0,0005	0,0082 ± 0,0010
Riviera olive oil (a)	0,0194 ± 0,0011	0,0146 ± 0,0010	0,0007 ± 0,0002
Riviera olive oil (b)	0,0173 ± 0,0006	$0,0127 \pm 0,0004$	$0,0023 \pm 0,0001$
Riviera olive oil (c)	0,0131 ± 0,0007	0,0125 ± 0,0001	0,0024 ± 0,0006
Virgin olive oil	$0,0155 \pm 0,0009$	$0,0295 \pm 0,0011$	$0,0065 \pm 0,0006$
Olive oil(for frying)	$0,0097 \pm 0,0005$	0,0236 ± 0,0006	0,0030 ± 0,0006
Sunflower oil (a)	0,0105 ± 0,0014	0,0076 ± 0,0002	0,0016 ± 0,0007
Sunflower oil (b)	0,0226 ± 0,0010	0,0071 ± 0,0001	0,0026 ± 0,0005
Sunflower oil (c)	0,0231 ± 0,0016	0,0107 ± 0,0002	0,0045 ± 0,0005
Sunflower oil (d)	0,0150 ± 0,0010	$0,0061 \pm 0,0006$	0,0025 ± 0,0001
Sunflower oil (e)	$0,0114 \pm 0,0022$	0,0144 ± 0,0011	0,0020 ± 0,0005
Corn oil (a)	0,0138 ± 0,0005	0,0039 ± 0,0003	0,0012 ± 0,0002
Corn oil (b)	0,0103 ± 0,0001	0,0195 ± 0,0010	0,0017 ± 0,0002
Corn oil (c)	0,0082 ± 0,0001	0,0352 ± 0,0020	0,0014 ± 0,0002

Table 2 Average of metal contents (mg/kg oil) obtained from every oil sample

\* mean; \*\* standard deviation.

466/2001, 2001); for cadmium, copper and zinc, no legislation currently exists. According to the results of Dugo *et al.*(2004), maize oils presented the highest mean concentration of Cd ( $4.90 \pm 1.0 \ \mu g/kg$ ) and rice oils the lowest ( $0.71 \pm 0.25 \ \mu g/kg$ ). Lead was also present in low concentrations, nut oils showed the highest mean value ( $55.61 \pm 9.05 \ \mu g/kg$ ) and rice oil the lowest ( $8.60 \pm 2.25 \ \mu g/kg$ ). FAO/WHO fixed an allowable daily intake of cadmium (II) at 7  $\mu g/kg$  od body weight (Crosby, 1977). Zinc (II) is an essential metal for the human body in minimal amounts, while it is dangerous in higher quantities and its presence in the soil reduces cadmium (II)

absorption by the plant (Choudhary *et al.*,1995). Lo Coco *et al.* (2003) determined 25.5-68.3 ng/g and 26.7-65.3 ng/g Zn (II) in different commercial samples of olive oils by using dPSA and ICP-AES, respectively.

The reproducibility obtained with acid extractions of oil samples was good and the results show that with this method it was possible to determine metals in edible vegetable oils with a precision estimated to below 1%. Acid extractions from the same oil sample at different times demonstrated that incubation in a shaking water bath for 2 h was sufficient to recover all the metal

Table 3			
Average of the metal contents	(mg/kg oil)	obtained from every	y oil sample

Edible Oils	Со	Cr	Pb
Soybean oil	0,0003* ± 0,0000**	0,0009 ± 0,0000	0,0000 ± 0,0000
Hazelnut oil	0,0000 ± 0,0000	0,0009 ± 0,0001	$0,0000 \pm 0,0000$
Almond oil	0,0040 ± 0,0001	0,0010 ± 0,0001	$0,0000 \pm 0,0000$
Natural olive oil	$0,0032 \pm 0,0001$	$0,0006 \pm 0,0001$	0,0019 ± 0,0001
Riviera olive oil (a)	$0,0003 \pm 0,0000$	$0,0009 \pm 0,0000$	0,0025 ± 0,0001
Riviera olive oil (b)	$0,0020 \pm 0,0001$	0,0009 ± 0,0001	$0,0000 \pm 0,0000$
Riviera olive oil (c)	$0,0000 \pm 0,0000$	$0,0006 \pm 0,0001$	$0,0024 \pm 0,0001$
Virgin olive oil	$0,0012 \pm 0,0002$	$0,0008 \pm 0,0000$	0,0074 ± 0,0008
Olive oil (for frying)	$0,0000 \pm 0,0000$	0,0007 ± 0,0001	0,0050 ± 0,0001
Sunflower oil (a)	0,0001 ± 0,0000	$0,0006 \pm 0,0001$	0,0016 ± 0,0040
Sunflower oil (b)	$0,0040 \pm 0,0001$	$0,0008 \pm 0,0001$	$0,0000 \pm 0,0000$
Sunflower oil (c)	$0,0010 \pm 0,0001$	0,0008 ± 0,0001	0,0012 ± 0,0006
Sunflower oil (d)	$0,0002 \pm 0,0001$	$0,0005 \pm 0,0001$	0,0026 ± 0,0001
Sunflower oil (e)	$0,0000 \pm 0,0000$	$0,0007 \pm 0,0001$	0,0013 ± 0,0003
Corn oil (a)	$0,0000 \pm 0,0000$	0,0006 ± 0,0001	$0,0000 \pm 0,0000$
Corn oil (b)	$0,0000 \pm 0,0000$	0,0006 ± 0,0001	$0,0000 \pm 0,0000$
Corn oil (c)	$0,0000 \pm 0,0000$	$0,0007 \pm 0,0000$	0,0000 ± 0,0000

\* mean; \*\* standard deviation.

Edible Oils	Cd	Ni	Zn
Soybean oil	0,0013* ± 0,0001**	0,0027 ± 0,0001	0,0348 ± 0,0020
Hazelnut oil	$0,0012 \pm 0,0001$	$0,0072 \pm 0,0004$	0,0185 ± 0,0025
Almond oil	$0,0003 \pm 0,0002$	$0,0254 \pm 0,0081$	0,2870 ± 0,0214
Natural olive oil	$0,0009 \pm 0,0001$	0,0013 ± 0,0000	0,0464 ± 0,0023
Riviera olive oil (a)	$0,0024 \pm 0,0001$	$0,0028 \pm 0,0002$	0,0454 ± 0,0022
Riviera olive oil (b)	$0,0016 \pm 0,0001$	$0,0017 \pm 0,0001$	0,0653 ±0,0038
Riviera olive oil (c)	$0,0033 \pm 0,0001$	0,0013 ± 0,0001	0,0475 ±0,0024
Virgin olive oil	$0,0028 \pm 0,0001$	$0,0030 \pm 0,0002$	0,0523 ± 0,0029
Olive oil (for frying)	$0,0021 \pm 0,0002$	0,0041 ± 0,0001	0,0521 ± 0,0031
Sunflower oil (a)	$0,0008 \pm 0,0001$	0,0033 ± 0,0002	0,0334 ± 0,0023
Sunflower oil (b)	$0,0019 \pm 0,0001$	$0,0019 \pm 0,0000$	0,0541 ± 0,0034
Sunflower oil (c)	$0,0007 \pm 0,0005$	$0,0015 \pm 0,0000$	0,0212 ± 0,0036
Sunflower oil (d)	$0,0007 \pm 0,0002$	$0,0032 \pm 0,0003$	0,0322 ± 0,0037
Sunflower oil (e)	$0,0045 \pm 0,0002$	$0,0060 \pm 0,0019$	0,0184 ± 0,0006
Corn oil (a)	$0,0002 \pm 0,0001$	0,0076 ± 0,0010	0,0229 ± 0,0047
Corn oil (b)	$0,0013 \pm 0,0001$	0,0096 ± 0,0010	0,0322 ± 0,0036
Corn oil (c)	$0,0012 \pm 0,0001$	$0,0015 \pm 0,0003$	0,0330 ± 0,0033

 Table 4

 Average of the metal contents (mg/kg oil) obtained from every oil sample

\*mean; \*\* standard deviation.

ions present in the oil samples. The analysis of the blanks demonstrated that there was no contamination of metal ions by the reagents or polypropylene containers. It is evident, especially for lead, that when the concentration was very low the results obtained were substantially influenced by noise and instrumental interference.

Lead is a naturally occurring element and is a common industrial metal that has become widespread in air, water, soil, and food. Lead contamination varies and manifests itself in other ways than in green plants. Lead has severe health effects even at relatively low levels in the body and can cross the placenta and damage developing fetal nervous systems (Yu et al., 2001). Lead and cadmium cause both acute and chronic poisoning, adverse effects on the kidney, liver, heart, vascular and immune systems (Heyes, 1997). Some micronutrients such as copper and zinc, are essential for plant growth and human nutrition at low doses but may also be toxic for humans, animals and plants at high doses. Copper and zinc are required in our diet because they exhibit a wide range of biological functions such as components of enzymatic and redox systems (McLaughlinet al., 1999). Environmental pollution due to copper arises from industrial and agricultural emissions. It is found in soil and water as a by-product from metal finishing in the processing industry and agricultural sources such as fertilizers and fungicidies (Namasivayam, & Senthilkumar, 1999). Chromium is a naturally occurring element found in rocks, plants, soil, and in volcanic dust and cases. Human are exposed when eating food, drinking water, and inhaling air that may contain chromium. Excessive amounts of Cr may be involved in the pathogenesis of some diseases such as lung and gastrointestinal cancers (Donais et al., 1999; Kubrakova *et al.*, 1994; Vique *et al.*, 1997). Cadmium is known as a principal toxic element, since it inhibits many life processes (Vetter, 1993; Vetter, 1994; Singh *et al.*, 1998). It can be taken up directly from water, and to some extent from air and via food, and it has a tendency to accumulate in both plants and animals.

## 4. CONCLUSION

We have demonstrated that the extraction with dilute nitric acid is a reliable method of sample preparation for the determination of copper and iron in edible vegetable oils by ICP-AES. It is very important to use containers of polypropylene because glass provides substantial contamination. Even when using very low quantities of oil samples it is possible to obtain good results. The proposed procedure allows for a reduction in the preparation time and the manipulation of the samples. Additionally, the final solution obtained can be analyzed directly by ICP-AES without all the instrumental problems. In addition, the metals may be introduced during the production process such bleaching, hardening, refining, as and deodorization or by contamination from the metal processing equipment and thus be suspended in the oil (Carlosena et al., 1999; Martin-Polvillo et al.,1994; Farhan et al.,1988).

All these metals have toxic potential, but the detrimental impact becomes apparent only after years of exposure. Monitoring of heavy metals in oil is essential in order to prevent excessive build-up of these metals in the human food chain. The companies to treat products before selling them to markets should take the appropriate measures during the production process.

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