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Metal Determinations in Olive Oil

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1. Introduction

It is widely known that trace metals have negative effects on the oxidative stability of olive oil. Natural composition of olive fruit, natural contamination from soil, fertilizers, industrial applications or highways near the plantations are the main sources of metals in olive oils. The olive oil may also be contaminated with the metals during the production process and contact with storage materials. The level of trace metals in olive oil is one of the quality parameters and also effective on oil oxidation and human health. Oxidation leading to the development of unfavorable odours and taste is one of the major reasons of deterioration of olive oils. The factors that most affect the rate of oxidation are the degree of unsaturation, the amount of oxygen, temperature, light and the presence of metals (mainly transition metals such as Fe and Cu) (Meira et al., 2011; Sikwese & Duodu, 2007). The trace metals enhance the rate of oxidation of edible oils by increasing the generation of free radicals from fatty acids or hydroperoxides. Benedet & Shibamoto observed that trace amounts of Fe, Cr, Pb and Cd contribute oxidative effects to lipid peroxidation (Benedet & Shibamoto, 2008).

The determination of metals has been a difficult analytical problem because of the hard organic content of the oil matrix. The analytical techniques used for metal determinations in oils are both emission and absorption spectrophotometry. ICP-OES (Allen et al., 1998; Angioni et al., 2006; Anthedimis et al., 2005; Costa et al., 2001; De Souza et al., 2005; Murillo et al., 1999; Zeiner et al., 2005), FAAS (Bati & Cesur, 2002; Carbonell et al., 1991; Köse Baran & Bağdat Yaşar, 2010; Nunes et al., 2011), ETA-AAS (Karadjova et al., 1998; Kowalewska et al., 1999; Zeiner et al., 2005), GFAAS (Allen et al., 1998; Ansari et al., 2009; Calapaj et al., 1988; Chen et al., 1999; Cindric et al., 2007; De Leonardis et al., 2000; Hendrikse et al., 1988, 1991; Lacoste et al., 1999; Martin-Polvillo et al., 1994; Matos Reyes & Campos, 2006; Mendil et al., 2009; Nash et al., 1983; Van Dalen, 1996), and ICP-MS (Benincasa et al., 2007; Bettinelli et al., 1995; Llorent-Martinez et al., 2011a, 2011b; Pereira et al., 2010; Wondimu et al., 2000) are the most commonly used techniques for the determination of metal contents in oils (Duyck et al., 2007).

In this chapter, recent determination techniques and sample pretreatment methods have been described and compared with each other. Additionally, a novel metal extraction procedure has been introduced in detail. In recent years, scientists have been interested in defining the bioavailable amount of metals more than total metal concentration. Taking into account this, fractionation and speciation analysis of metals in oil samples have also been discussed in the chapter.

2. Sample pre-treatment

The accurate determination of trace metals in olive oil is an analytical challenge due to their low concentration and the difficulties that arise because of the high organic content. Due to the high organic content, sample pretreatment is a critical step and frequently necessary in olive oil analysis. Sample pretreatment step provides the decomposition of organic matrix or the extraction of metals without matrix decomposition. On the other hand, oil sample can be diluted in a suitable solvent or emulsified with an appropriate emulsifier in a rapid pretreatment for direct determinations. The atomic spectrometers are the most commonly used devices but have some problems such as the reduced stability of the analytes in the solution, requirement of organometallic standards, the use of dangerous organic solvents or sample digestion with an acid or acid mixture (Nunes et al., 2011).

2.1 Acid digestion

Digestion procedures are regularly carried out with either open vessels using acid, acid mixture or basic reagents on hot plates or open- and closed-vessel microwave ovens. The decomposition in open system is hard, time consuming and prone to systematic error sources, i.e. contamination or analyte losses. In case of using microwave radiation, the high cost of instrumentation and dilution of the sample can be considered as disadvantages in the microwave assisted digestion system. Although the amount of sample in vessels is limited due to the generation of gaseous reaction products that can increase of pressure, the use of closed high-pressure vessels is appropriate for efficient sample digestion. On the other hand, in the use of open-focused microwave ovens, the advantages are decreasing the risk to the operator, possible introduction of reagents during procedure, opportunity to digest larger amounts of sample and low cooling time (Sant'Ana et al., 2007).

Microwave-assisted digestion has been performed to dissolve the oil sample for elemental analysis in a large number of papers (Angioni et al., 2006; Ansari et al., 2009; Levine et al., 1999; Llorent-Martinez et al., 2011a, 2011b; Mendil et al., 2009; Sant'Ana et al., 2007), while focused microwave assisted digestion for the same purpose has been employed in a few papers (Sant'Ana et al., 2007). As shown in Table 1, some investigation have been done on microwave digestion for olive oil using various procedures.

2.2 Dry ashing

In general, ashing methods may provide lower analyte recovery and exhibit poorer accuracy compared to acid digestion methods. Although dry ashing procedures are effective, they are time consuming and can often result in loss of analyte species that could occur during the preparation of the sample. Oil is decomposed by high-temperature dry ashing, subsequently the ash is dissolved in an acidic aqueous medium and the metal content of the aqueous phase can be measured by various detection techniques such as AAS, adsorptive stripping voltammetry (AdSV) and derivative potentiometric stripping analysis (dPSA) (Abbasi et al., 2009; Carbonell et al., 1991; Lo Coco et al., 2003). There are limited researches for metal determinations in oils after dry ashing of olive oil (Lo Coco et al., 2003).

Microvawe digestion procedure	Reagent	Metals determined	Reference
130 °C 10 min. 140 psi, 150 °C 10 min. 200 psi, 10 min. cooling, 160 °C 20 min. 200 psi	HNO ₃	Mg, Ca, Cr, Fe, Mn, Cu, Ni, Zn, Cd, Pb	Bağdat Yaşar & Güçer, 2004
2 min. for 250 W, 2 min. for 0 W, 6 min. for 250 W, 5 min. for 400 W, 8 min. for 550 W, vent.: 8 min.	HNO ₃ -H ₂ O ₂	Fe, Mn, Zn, Cu, Pb, Co, Cd, Na, K, Ca, Mg	Mendil et al., 2009
250 W 2 min., 0 W 1 min., 250 W 2 min., 600 W 1 min., 400 W 5 min., vent.: 3min.	HNO ₃ -H ₂ O ₂	Ca, Fe, K, Mg, Na, Zn, Al, Co, Cu, Mn, Ni, Cr, Pb	Cindric et al., 2007
25 _i -90 _f °C 5 min. 700 W, 90 _i -90 _f °C 3 min. 600 W, 90 _i -170 _f °C 10 min. 600 W, 170 _i -170 _f °C 7 min. 600 W	HNO ₃	Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Ti, Tl, V	Llorent-Martinez et al., 2011a, 2011b
300 W (83%) for 15 min., 600 W (75%) for 10 min., 1200 W (65%) for 15 min., 300 W (83%) for 5 min.	HNO ₃ -H ₂ O ₂	Cd, Cu, Pb, Zn	Angioni et al., 2006
750 W 90 °C 6 min., 750 W 90 °C 4 min., 1000 W 180 °C 8 min., 1000 W 180 °C 15 min. (35 bar), vent.: 20 min	HNO ₃ -H ₂ O ₂	Cu, Fe, Ni, Zn	Nunes et al., 2011
250 W, 4 min., 0 W 4 min., 250 W 5 min., 400 W 7 min., 700 W 6 min., 350 W 5 min.	HNO ₃	Be, Mg, Ca, Sc, Cr, Mn, Fe, Co, Ni, As, Se, Sr, Y, Cd, Sb, Sm, Eu, Gd	Benincasa et al., 2007

i: initial ; f: final

Table 1. The summary of microwave digestion procedures for various metals in olive oil.

2.3 Extraction

Sample preparation involves acid extraction (Anwar et al., 2004; De Leonardis et al., 2000; Dugo et al., 2004; Jacob & Klevay, 1975), solid phase extraction (SPE) (Batı & Cesur, 2002) or extraction with special agents (Köse Baran & Bağdat Yaşar, 2010).

After the extraction of metals from oil with nitric acid, hydrochloric acid or acid mixture, the extracts are analyzed. Despite the fact that extraction method has the same advantage both in the separation and preconcentration of metals in oil samples, the recoveries are not satisfactory for many metals in most cases. Batı and Cesur described another method for the preconcentration and separation of copper in edible oils, based on using a solid Pb-piperazine-dithiocarbamate complex for extraction and a potassium cyanide solution for back extraction (Batı & Cesur, 2002).

Anwar et al. reported a simple acid-extraction method for the determination of trace metals in oils and fats. The method has been performed with the use of ultrasonic intensification and successfully applied for accurate determination of iron, copper, nickel and zinc in oils (Anwar et al., 2004). Many extraction procedures are available in literature, the summary of these is given in Table 2.

Extraction method	Metals determined	Detection technique	Notes	Reference
Extraction with 10% HNO ₃	Fe, Cu	GF-AAS	¹ Acc.% 94±23 (Cu); 97±12 (Fe)	De Leonardis et al., 2000
Extraction with CCl ₄ + 2 N HNO ₃ (ultrasonic intensification)	Fe, Cu, Ni, Zn	FAAS	² Rec.% 92-98 (Fe); 91-100 (Cu); 92-97 (Ni); 93-101 (Zn)	Anwar et al., 2004
Extraction with 35% H ₂ O ₂ and 36% HCl (30 min., 90 °C)	Cd, Cu, Pb, Zn	dPSA	Rec.% 96.5±2.1 (Cd); 97.0±2.7 (Cu); 95.0±1.8 (Pb); 93.5±1.7 (Zn)	Dugo et al., 2004
Extraction with conc. HCl	Cu	Ad-SSWV	³ LOD: 0.49 ng mL ⁻¹	Galeano Diaz et al., 2006
Extraction with conc. HNO ₃ and 6% H ₂ O ₂	Cu, Ni	UV-Vis spec.	Rec.% 90-118 (Cu); 96-100 (Ni)	Hussain Reddy et al., 2003
Extraction with 10% HNO ₃ (50 Hz, 60 s)	Cu, Fe, Mn, Co, Cr, Pb, Ni, Cd, Zn	ICP-AES	⁴ RSD%: < 10 (Cu); 5 (Fe); 15 (Mn); 8 (Co); 10 (Cr); 20 (Pb); 5 (Cd); 16 (Ni); 11 (Zn)	Pehlivan et al., 2008
Extraction with CCl ₄ and 2 N HNO ₃ after pretreatment with conc. HNO ₃ (ultrasonic bath, 30 °C)	Fe, Cu, Zn, Ni	FAAS	Rec.% 96.5-97.5 (Fe); 96.5-97.1 (Cu); 95.8-97.5 (Ni); 96.0-97.8 (Zn)	Anwar et al., 2003
Pb-piperazinedithiocarbamate SPE and KCN back-extraction	Cu	FAAS	Rec.% 91-97	Batı & Cesur, 2002
Zn-piperazinedithiocarbamate SPE	Cd	FAAS	Rec.% 93.1-100	Yağan Aşçı et al., 2008
Ultrasonic-Assisted extraction with conc. HNO ₃ and H ₂ O ₂ (35 kHz)	Cu, Fe, Ni	FAAS and ETAAS	Rec.% 95.9-98.3 (Cu); 95.7-98.2 (Fe); 95.2-97.5 (Ni)	Ansari et al., 2008
Ultrasonic-Assisted extraction with conc. HCl and 30% H ₂ O ₂	Cu, Pb	SCP	Rec.% 82-107 (Cu); 84-105 (Pb)	Cypriano et al., 2008
Extraction with <i>N,N'</i> -bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminato (LDM)	Fe, Cu	FAAS	Rec.% 100.2±5.6 (Fe); 99.4±2.8 (Cu)	Köse Baran & Bağdat Yaşar, 2010

¹Acc.: Accuracy; ²Rec.: Recovery; ³LOD: Limit of detection; ⁴RSD: Relative standard deviation

Table 2. The extraction methods used for metal determination in vegetable oils

A Schiff base has been suggested for the extraction of metals from oils as an appropriate chelating agent under the optimum extraction conditions (Köse Baran & Bağdat Yaşar, 2010). In recent analytical applications, Schiff bases have been used in order to form complexes due to their good complexing capacity with metals (Afkhami et al., 2009; Ashkenani et al., 2009; Ghaedi et al., 2009; Khedr et al., 2005; Khorrami et al., 2004; Köse Baran & Bağdat Yaşar, 2010; Kurşunlu et al., 2009; Mashhadizadeh et al., 2008; Shamspur et

al., 2003; Tantarú et al., 2002; Ziyadanoğulları et al., 2008). The chemists have attended to the Schiff bases and their metal complexes because of their widespread applications in biological systems and industrial uses (Issa et al., 2005; İspir, 2009; Kurtaran et al., 2005; Li et al., 2007; Mohamed, 2006; Neelakantan et al., 2008; Prashanthi et al., 2008; Sharaby, 2007).

Although most techniques for metal determinations in edible oils require sample digestion, dilution or emulsification, the improved method can be employed for the same purpose without digestion. The procedure is based on efficient extraction of metals from oil to aqueous solution, and the determination of metals in aqueous phase by FAAS. The proposed approach has been applied for Fe, Cu, Ni and Zn successively. This method includes two main steps. Metal complexes with Schiff bases shown in Fig. 1 were investigated spectrophotometrically as a first step. In this step, the investigation of the complexation reaction as a driving force for the extraction is necessary to decide the appropriate pH and the equilibrium time in terms of complexation efficiency.

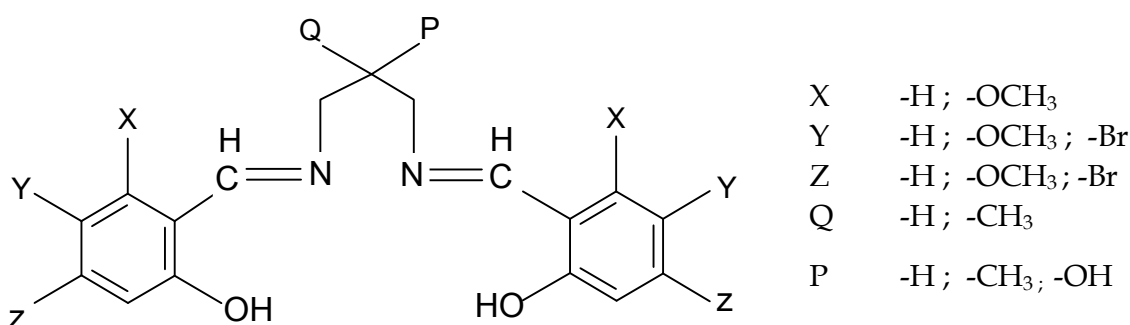


Fig. 1. Chemical structure of Schiff base used in the extractions

As a second step, the experimental conditions affecting the extraction efficiency of metals should be researched. In the procedure of metal extraction with a Schiff base, the optimization of parameters -the ratio of Schiff base solution volume to oil mass, the stirring time and the temperature- for the metal extractions has been achieved by carrying out central composite design (CCD) as an optimization method.

As shown in Table 3, the CCD consisting of a combination of 2³ full factorial design and a star design was used, in which three independent factors were converted to dimensionless ones (x_1, x_2, x_3) with the coded values at 5 levels: -1.682, -1, 0, +1, +1.682.

Factors	Levels				
	-1.682	-1	0	+1	+1.682
x_1 (1 st factor) V_{LDM} / m_{oil} ratio (mL g ⁻¹)	0.159	0.5	1	1.5	1.841
x_2 (2 nd factor) Stirring time (minute)	9.56	30	60	90	110.46
x_3 (3 rd factor) Temperature (°C)	13.18	20	30	40	46.82

Table 3. Variables, levels and the values of levels used in CCD (Köse Baran & Bağdat Yaşar, 2010)

Fifteen experiments should be done in a CCD. Additionally, to estimate the experimental error, replications of factor combinations are necessary at the center point (the level, 0). Experiment at the center point has been repeated five times. The total number of experiments in the CCD with three factors then amounts to 20 (Morgan, 1991; Otto, 1999). Accordingly, 20 experiments given in Table 4 were carried out in the extent of the CCD optimization procedure.

Experiment no.	Coded values of levels		
	V_{LDM} / m_{oil} ratio (mL g ⁻¹) x_1	Stirring time (min.) x_2	Temperature (°C) x_3
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1
9	0	0	0
10	-1,682	0	0
11	+1,682	0	0
12	0	-1,682	0
13	0	+1,682	0
14	0	0	-1,682
15	0	0	+1,682
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

Table 4. The coded values of levels for the experiments in the extent of CCD

Organo-metallic standards in oil (Conostan code number; 354770 for iron, 687850 for copper) were used in CCD and metal concentrations of oil standards were fixed to be a certain concentration. The metal concentrations of the extracts gained from each experiment were determined by FAAS. The obtained results were used in order to establish recovery values for the extraction of metals from oil. The response values (y) were calculated from experimentally obtained recovery percentages. The empirical equations were developed by means of response values (Morgan, 1991; Otto, 1999). The following y equations were constructed based on the b values which were calculated by applying to the appropriate matrixes.

$$y = b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \quad (1)$$

New corresponding equations were obtained by equalization of the derivatives of y equation in terms of x_1, x_2, x_3 to zero and solved using software to provide optimum extraction conditions. Optimum conditions are variable depending on the structure of Schiff base and significant metal. The found optimum conditions are given in Table 5 when LDM (Q and P = CH₃; X, Y and Z = H) was used as a Schiff base. The recovery values for the extraction of Cu and Fe from oil under the optimum experimental conditions were found to be 99.4(±2.8) and 100.2(±5.6)%, respectively (n=10). To test the applicability of the improved procedure, it was applied on spiked olive, sunflower, corn and canola oils. The recovery percentages were varied between 97.2-102.1 for Cu and 94.5-98.6 for Fe (Köse Baran & Bağdat Yaşar, 2010).

Metal	Optimum Conditions		
	V_{LDM} / m_{oil} ratio (mL g ⁻¹)	Stirring time (min.)	Temperature (°C)
Cu	0.76	73	31
Fe	1.19	67	28

Table 5. Optimum extraction conditions for determination of Cu and Fe in edible oils (Köse Baran & Bağdat Yaşar, 2010)

The improved determination strategy after the extraction with Schiff bases has main advantages like independency from hard oil matrix, elimination of explosion risk during decomposition, no requirement for expensive instruments, high accuracy, sensitivity, rapidity and cheapness.

3. Direct determination

The direct determination of metals in oils can be carried out by sample solubilization in an organic solvent, an emulsification procedure in aqueous solutions in the presence of emulsifiers such as Triton X-100 or a solid sampling strategy.

3.1 Dilution with organic solvent

The procedure of the dilution with organic solvents is an easy way to sample pretreatment before detection, but has some requirements: special devices for sample introduction e. g. for FAAS (Bettinelli et al., 1995), the addition of oxygen as an auxiliary gas in ICP-OES or ICP-MS (Costa et al., 2001). The volatile organic solvents have been directly introduced into ICPs for many years, but this can cause plasma instability, less sensitivity, less precision and high cost. Al, Cr, Cd, Cu, Fe, Mn, Ni and Pb contents of olive oil were investigated using diethyl ether, methyl isobutyl ketone (MIBK), xylene, heptane, 1,4-dioxane as solvent and N,N-hexamethylenedithiocarbamic acid, hexamethylenammonium (HMDC-HMA) salt as a modifier by ETAAS (Karadjova et al., 1998). A transverse heated filter atomizer (THFA) was employed for the direct determination of Cd and Pb in olive oil after sample dilution with n-heptane (Canario & Katskov, 2005). Moreover, Martin-Polvillo et al. (1994) and List et al. (1971) determined trace elements in edible oils based on the direct aspiration of the samples, diluted in MIBK. In another research, the mixture of 2%lecithin-cyclohexane was used to introduce the oil samples to a polarized Zeeman GFAAS (Chen et al., 1999). Van Dalen was

also used lecithin and the organopalladium modifier solutions for the injection of the edible oils (Van Dalen, 1996).

3.2 Emulsification

Taking into account parameters such as economy, safety, environment, time, and low risk of contamination, emulsification appears beneficial over microwave assisted acid digestion. On the other hand, optimization of the particle size effect, slurry concentration and homogeneity are necessary in order to obtain good precision and recoveries with slurry techniques. In spite of optimization, complete destruction of the sample matrix in plasma and then liberation of analyte from the sample matrix are not always succeeded, causes unsatisfactory results. An alternative technique for introduction of oil sample directly into ICP is the on-line emulsification (Anthemidis et al., 2005). Direct introduction of oil samples in the form of emulsion into ICP facilitates the spray chamber and plasma torch owing to no need of extra oxygen or sophisticated desolvation device. In such a case, the use of stable emulsions with proper surfactant concentration is very important (Anthemidis et al., 2005).

Emulsification as sample preparation has been performed for the determination of trace metals in vegetable oils by ICP-OES (De Souza et al., 2005; Murillo et al., 1999), ICP-MS (Castillo et al., 1999; Jimenez et al., 2003), FAAS (List et al., 1971) and GF-AAS (Lendinez et al., 2001). Additionally, the use of microemulsion as sample preparation for vegetable oil analysis by High-Resolution Continuum Source FAAS (HR-CS FAAS) has been described by Nunes et al. (2011). The determination of Zn, Cd and Pb in vegetable oils by electrothermal vaporization in combination with ICP-MS (ETV-ICP-MS) was described in literature (Huang et al., 2001).

3.3 Direct solid sampling

Direct introduction of oil samples into the graphite furnace by solid sampling strategy is rarely used, providing an alternative methodology. Due to technical improvements in spectrophotometer and software capabilities of modern instrumentation, this method has not been entirely accepted (Sardans et al., 2010). Direct solid sampling has some advantages such as no sample dilution, satisfactory LOD levels, calibration probability with aqueous analytical solutions, simple analysis and no sample digestion or extraction. Other advantages of this method are reduced time and cost, required little amount of sample and the achievement of high sensitivity. Additionally, it reduces the risk of contamination due to the nonexistence of sample preparation and use of chemical reagents. Some disputes against the method are the difficulty of introducing small sample masses, faulty measurement of the results due to the heterogeneity of some natural samples and the limiting linear working range of AAS (Sardans et al., 2010). Despite these restrictions, direct solid sampling is a reasonable alternative for the determination of the total content of metals in oils, since it needs almost no sample preparation. A method for the direct determination of Ni and Cu in vegetable oils by GFAAS using the solid sampling strategy has been reported without sample dilution by Matos Reyes et al. (2006).

3.4 Flow injection

Various detection techniques like ETAAS, FAAS, ICP-OES, ICP-MS, voltammetry have been utilized for metal determination in oils. However, all of them have the need for sample

pretreatment procedures in common like: wet digestion, dry ashing, extraction and dilution with organic solvent in order to eliminate hard organic matrix. In the processing large numbers of samples, flow injection analysis (FIA) systems can be preferred for sample pretreatment. The FIA system for oil analysis is frequently based on the on-line preparation of oil-in-water emulsions by using ultrasonic bath with serious drawbacks in efficient preparation of stable emulsions. By this way, more concentrated emulsions (high oil concentration) can be introduced into the plasma and thereby the LODs were improved. A limited number of researches related to metal determination in oils by FIA systems have been presented. Jimenez et al. succeeded multi-element determination in virgin olive oil by flow injection ICP-MS using with HNO₃ and Triton X-100 as emulsifying agents (Jimenez et al., 2003). A magnetic-stirring micro-chamber has been developed for on-line emulsification and has been successfully employed by Anthemidis et al. to detect Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, Mg, Mn, Ni, Pb, Tl and Zn in olive oil using flow injection ICP-OES (Anthemidis et al., 2005). The low concentration of analyte in the sample analysed and difficulty of obtaining stable emulsions with rich oil content were reported as the main problems. On-line emulsion preparation procedure was suggested as simpler, more effective, less time consuming, less labor intensive, less matrix interferences and less contamination risk over the other direct sample introducing procedures. The direct determination of Cu and Fe in edible oils based on the flow injection standard addition method by FAAS was performed without sample dilution in a previous study (Carbonell et al., 1991).

As mentioned above, various pretreatment procedure and detection techniques have been employed for the total determination of metals in olive oil. The researchers have dealt with metallic contents of olive oils during last few decades. As can be seen in Table 6, the concentration range of total amount is given for many metals.

Metal	Concentration ($\mu\text{g g}^{-1}$) (* ng g^{-1})		References
	Minimum	Maximum	
Fe	12.5*	139.0	(Anthemidis et al., 2005; Benincasa et al., 2007; Buldini et al., 1997; Calapaj et al., 1988; Cindric et al., 2007); De Leonardis et al., 2000; Llorent-Martinez et al., 2011a, 2011b; Martin-Polvillo et al., 1994; Mendil et al., 2009; Nunes et al., 2011; Pehlivan et al., 2008; Zeiner et al., 2005)
Cu	1.7*	4.51	(Angioni et al., 2006; Anthemidis et al., 2005; Buldini et al., 1997; Calapaj et al., 1988; Castillo et al., 1999; Cindric et al., 2007; De Leonardis et al., 2000; Galeano Diaz et al., 2006; Jimenez et al., 2003; Karadjova et al., 1998; Llorent-Martinez et al., 2011a, 2011b; Martin-Polvillo et al., 1994; Mendil et al., 2009; Nunes et al., 2011; Pehlivan et al., 2008; Zeiner et al., 2005)
Ni	10.6*	2.26	(Benincasa et al., 2007; Buldini et al., 1997; Calapaj et al., 1988; Castillo et al., 1999; Cindric et al., 2007; Nunes et al., 2011; Zeiner et al., 2005)
Zn	0.6*	4.61	(Angioni et al., 2006; Cindric et al., 2007; Lo Coco et al., 2003; Mendil et al., 2009; Nunes et al., 2011; Zeiner et al., 2005)

Mn	0.7*	0.15	(Anthemidis et al., 2005; Benincasa et al., 2007; Calapaj et al., 1988; Castillo et al., 1999; Cindric et al., 2007; Jimenez et al., 2003; Karadjova et al., 1998; Llorent-Martinez et al., 2011a; Mendil et al., 2009; Pehlivan et al., 2008; Zeiner et al., 2005)
Pb	0.42*	0.032	(Calapaj et al., 1988; Canario & Katskov, 2005; Castillo et al., 1999; Jimenez et al., 2003; Llorent-Martinez et al., 2011a; Mendil et al., 2009; Martin-Polvillo et al., 1994)
Co	0.23*	5.45	(Benincasa et al., 2007; Calapaj et al., 1988; Castillo et al., 1999; Cindric et al., 2007; Mendil et al., 2009; Zeiner et al., 2005)
Cd	0.6*	0.15	(Angioni et al., 2006; Benincasa et al., 2007; Calapaj et al., 1988; Canario & Katskov, 2005; Castillo et al., 1999; Mendil et al., 2009; Yağan Aşçı et al., 2008)
Cr	0.012	2.00	(Anthemidis et al., 2005; Benincasa et al., 2007; Calapaj et al., 1988; Castillo et al., 1999; Llorent-Martinez et al., 2011a)
V	0.005	0.46	(Castillo et al., 1999); (Llorent-Martinez et al., 2011a)
Ge	0.03	0.04	(Castillo et al., 1999)
Zr	0.01	0.04	(Castillo et al., 1999)
Ba	4.9*	0.7	(Castillo et al., 1999; Jimenez et al., 2003; Llorent-Martinez et al., 2011a)
Al	0.030	1.11	(Anthemidis et al., 2005; Cindric et al., 2007; Jimenez et al., 2003; Karadjova et al., 1998; Martin-Polvillo et al., 1994; Zeiner et al., 2005)
Be	0.118*	0.178*	(Benincasa et al., 2007)
Sc	49.94*	747.9*	(Benincasa et al., 2007)
As	1.248*	26.65*	(Benincasa et al., 2007)
Se	1.47*	6.78*	(Benincasa et al., 2007)
Sr	1.52*	48.9*	(Benincasa et al., 2007)
Y	0.082*	0.331*	(Benincasa et al., 2007)
Sb	0.194*	0.411*	(Benincasa et al., 2007)
Sm	0.004*	0.226*	(Benincasa et al., 2007)
Eu	0.004*	0.021*	(Benincasa et al., 2007)
Gd	0.003*	0.094*	(Benincasa et al., 2007)
Sn	0.126	0.159	(Calapaj et al., 1988)
Mg	0.056	4.61	(Bağdat Yaşar & Güçer, 2004; Benincasa et al., 2007; Cindric et al., 2007; Mendil et al., 2009; Zeiner et al., 2005)
Ca	0.63	76.0	(Anthemidis et al., 2005; Benincasa et al., 2007; Cindric et al., 2007; Mendil et al., 2009; Zeiner et al., 2005)
K	0.05	2.14	(Cindric et al., 2007; Mendil et al., 2009; Zeiner et al., 2005)
Na	8.7	38.03	(Cindric et al., 2007; Mendil et al., 2009; Zeiner et al., 2005)

Table 6. The metal levels for olive oils.

4. Speciation and fractionation

Fractionation was defined as “the process of classification of analyte or a group of analytes from a certain sample according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties”, and speciation of an element was also defined as “distribution of an element amongst defined chemical species in a system” by Templeton et al. (2000). The physicochemical form of an element, i.e. the actual species found in exposure medium and in the different body fractions, is frequently determinant in the evaluation of its bioavailability and toxicity (Flaten, 2002). An element can be found in various species: anionic or cationic inorganic forms, inorganic compounds, complex compounds with protein, peptide etc. Some organometallic compounds are much more toxic than the ions of the corresponding inorganic compounds. Hg, Pb and Sn obey this rule, for example, methyl-Hg and inorganic Hg are both toxic, but methyl-Hg show more toxicity than other (Templeton et al., 2000). In contrast to this, in the case of As and Se, most organo-arsenicals are less toxic than inorganic As species, organic forms of Se are ordinarily less toxic than Se(IV) (Kot & Namiesnik, 2000).

The determination of the total amount of an element in samples cannot give adequate information for understanding its bioavailability or toxicity, that's why the fractionation and speciation of metals in oils are increasingly gaining importance. The fractionation and speciation analysis are more informative than total element determinations for all type of samples.

In general, many works dealing with the total amount of elements in oil samples are reported, but fractionation and/or speciation analysis in vegetable oils are less common in literature. To the best of our knowledge, magnesium fractionation analysis in olive and olive oil was cited firstly in 2004. The improvement of an analytical scheme for fractionation of magnesium in olive products and also the determination of Mg amounts absorbed in stomach and intestine was achieved by Bağdat Yaşar & Güçer (2004). It was reported that 3.37-8.47% of Mg was absorbed in the stomach (ionic and polar groups) and the remaining percentage of Mg was absorbed in the intestine (molecular and complexed structures) in olive oil. As can be seen, the Mg fraction in olive oil is almost absorbable in the intestine. This study can be accepted as a preliminary step for fractionation studies and the fractionation and/or speciation approach for other elements will be described in the future.

5. Detection techniques

Various researchers deal with determination of metals in oils at trace, ultra-trace levels using spectrometric and electrometric techniques. Mentioned detection techniques may be combined with some chromatographic systems. Oils have been analyzed for different metals using atomic absorption spectrometer (FAAS and GFAAS), inductively coupled plasma optical emission spectrometer (ICP-OES), inductively coupled plasma mass spectrometer (ICP-MS). ICP techniques have become more popular since the early 1990s. Although the use of AAS (flame, graphite furnace, hydride generation and cold vapour) has declined during the same period, it is still the most widely used technique (Rose et al., 2001).

Each technique has some special requirements, advantages and disadvantages according to its basic principle. GF-AAS is a sensitive, proper for direct introduction of oil samples in the form of emulsion and does not require a large amount of sample. FAAS and ICP-MS have a requirement of sample pretreatment, but ICP-MS is more sensitive and expensive when compared with FAAS. There are scarce researches dealing with oil samples related to voltammetric and potentiometric techniques such as Ad-SSWV, dPSA (Abbasi et al., 2009; Cypriano et al., 2008; Dugo et al., 2004; Galeano Diaz et al., 2006; Lo Coco et al., 2003).

6. Conclusion

Trace quantities of some metals are naturally present in olive oil. It could be possible to determine the levels of different trace metals with the help of precise and accurate analytical methods. In many cases, a sample pretreatment process is necessary to eliminate the oil matrix prior to the introduction of the sample into the instrument. A direct determination is also possible by sample solubilization in an organic solvent, an emulsification procedure or a solid sampling strategy when ETAAS, GF-AAS or ICP are used for the analysis of edible oils. Microwave-assisted wet digestion sample pretreatment is also employed combined with sensitive detection techniques. An alternative technique can be achieved efficiently and precisely by FAAS after the extraction of metals with a Schiff base ligand.

7. Abbreviations

AAS	Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
GF-AAS	Graphite Furnace Atomic Absorption Spectrometry
ETAAS	Electrothermal Atomic Absorption Spectrometry
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
Ad-SSWV	Adsorptive Stripping Square Wave Voltammetry
dPSA	Derivative Potentiometric Stripping Analysis
SCP	Stripping Chronopotentiometry

8. References

- Abbasi, S.; Allahyari, M.; Taherimaslak, Z.; Nematollahi, D. & Abbasi, F. (2009). New Determination of Lead in Edible Oil and Water Samples by High Selective Adsorptive Stripping Voltammetry with SPADNS. *International Journal of Electrochemical Science*, Vol.4, (March 2009), pp. 602-613, ISSN 1452-3981
- Afkhami, A.; Abbasi-Tarighat, M. & Khanmohammadi, V. (2009). Simultaneous Determination of Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} Ions in Foodstuffs and Vegetables with

- A New Schiff Base using Artificial Neural Networks. *Talanta*, Vol.77, (July 2008), pp. 995-1001, ISSN 0039-9140
- Allen L. B., Siitonen, P. H. & Thompson, H. C. (1998). Determination of Copper, Lead, and Nickel in Edible Oils by Plasma and Furnace Atomic Spectroscopies. *Journal of the American Oil Chemists Society*, Vol.75, No.4, (October 1997), pp. 477-481, ISSN 0003-021X
- Angioni, A.; Cabitza, M.; Russo, M. T. & Caboni, P. (2006). Influence of Olive Cultivars and Period of Harvest on the Contents of Cu, Cd, Pb, and Zn in Virgin Olive Oils. *Food Chemistry*, Vol.99, (August 2005), pp. 525-529, ISSN 0308-8146
- Ansari, R.; Kazi, T. G.; Jamali, M. K.; Arain M. B.; Sherazi, S. T., Jalbani, N. & Afridi, H. I. (2008). Improved Extraction Method for the Determination of Iron, Copper, and Nickel in New Varieties of Sunflower Oil by Atomic Absorption Spectroscopy. *Journal of AOAC International*, Vol.91, No.2, (November 2008), pp. 400-407, ISSN 1060-3271
- Ansari, R.; Kazi, T. G.; Jamali, M. K.; Arain M. B.; Wagan, M. D.; Jalbani, N.; Afridi, H. I. & Shah, A. Q. (2009). Variation in Accumulation of Heavy Metals in Different Varieties of Sunflower Seed Oil with The Aid of Multivariate Technique. *Food Chemistry*, Vol.115, (November 2007), pp. 318-323, ISSN 0308-8146
- Anthemidis, A. N.; Arvanitidis, V. & Stratis, J. A. (2005). On-line Emulsion Formation and Multi-element Analysis of Edible Oils by Inductively Coupled Plasma Atomic Emission Spectrometry. *Analytica Chimica Acta*; Vol.537, (January 2005), pp. 271-278, ISSN 0003-2610
- Anwar, F.; Kazi, T.G.; Jakharani, M.A.; Sultana, R. & Sahito, S.R. (2003). Improved Extraction Method for the Determination of Fe, Cu, Zn and Ni in Fat Samples using Atomic Absorption Spectrophotometer. *Journal of the Chemical Society of Pakistan*, Vol.25, No.3, (April 2003), pp. 210-214, ISSN 0253-5106
- Anwar, F.; Kazi, T.G.; Saleem, R. & Bhangar, M.I. (2004). Rapid Determination of Some Trace Metals in Several Oils and Fats. *Grasas y Aceites*, Vol.55, Fasc.2, (September 2003), pp. 160-168, ISSN 0017-3495
- Ashkenani, H.; Dadfarnia, S.; Shabani, A. M. H.; Jaffari, A. A. & Behjat, A. (2009). Preconcentration, Speciation and Determination of Ultra Trace Amounts of Mercury by Modified Octadecyl Silica Membrane Disk/Electron Beam Irradiation and Cold Vapor Atomic Absorption Spectrometry. *Journal of Hazardous Materials*, Vol.161, (March 2008), pp. 276-280, ISSN 0304-3894
- Bağdat Yaşar, S. & Güçer, Ş. (2004). Fractionation Analysis of Magnesium in Olive Products by Atomic Absorption Spectrometry. *Analytica Chimica Acta*, Vol.505, (May 2003), pp. 43-49, ISSN 0003-2670
- Bati, B. & Cesur H. (2002). Determination of Copper in Edible Oils by Atomic Absorption Spectrometry after Lead Piperazinedithiocarbamate Solid-Phase Extraction and Potassium Cyanide Back-Extraction. *Analytical Sciences*, Vol.18, (August 2002), pp. 1273-1274, ISSN 0910-6340
- Benedet, J. A. & Shibamoto T. (2008). Role of Transition Metals, Fe(II), Cr(II), Pb(II), and Cd(II) in Lipid Peroxidation. *Food Chemistry*, Vol.107, (July 2007), pp. 165-168, ISSN 0308-8146

- Benincasa, C.; Lewis, J.; Perri, E.; Sindona, G. & Tagarelli, A. (2007). Determination of Trace Element in Italian Virgin Olive Oils and Their Characterization According to Geographical Origin by Statistical Analysis. *Analytica Chimica Acta*, Vol.585, (December 2006), pp. 366-370, ISSN 0003-2670
- Bettinelli, M.; Spezia, S.; Baroni, U. & Bizzari, G. (1995). Determination of Trace Elements in Fuel Oils by Inductively Coupled Plasma Mass Spectrometry after Acid Mineralization of the Sample in a Microwave Oven. *Journal of Analytical Atomic Spectrometry*, Vol.10, (April 1995), pp. 555-560, ISSN 0267-9477
- Buldini, P. L.; Ferri, D. & Sharma, J. L. (1997). Determination of Some Inorganic Species in Edible Oils and Fats by Ion Chromatography. *Journal of Chromatography A*, Vol.789, pp. 549-555, ISSN 0021-9673
- Calapaj, R.; Chiricosta, S.; Saija, G. & Bruno, E. (1988). Method for the Determination of Heavy Metals in Vegetable Oils by Graphite Furnace Atomic Absorption Spectroscopy. *Atomic Spectroscopy*, Vol.9, No.4, pp. 107-109, ISSN 0195-5373
- Canario, C. M. & Katskov, D. A. (2005). Direct Determination of Cd and Pb in Edible Oils by Atomic Absorption Spectrometry with Transverse Heated Filter Atomizer. *Journal of Analytical Atomic Spectrometry*, Vol.20, (September 2005), pp. 1386-1388, ISSN 0267-9477
- Carbonell, V.; Mauri, A.R.; Salvador, A. & DeLaGuardia, M. (1991). Direct Determination of Copper and Iron in Edible Oils using Flow Injection Flame Atomic Absorption Spectrometry. *Journal of Analytical Atomic Spectrometry*, Vol.6, (June 1991), pp. 581-584, ISSN 0267-9477
- Castillo, J.R.; Jimenez, M.S. & Ebdon, L. (1999). Semiquantitative Simultaneous Determination of Metals in Olive Oil using Direct Emulsion Nebulization. *Journal of Analytical Atomic Spectrometry*, Vol.14, (March 1999), pp. 1515-1518, ISSN 0267-9477
- Chen, S.S.; Chen, C.M.; Cheng, C.C. & Chou, S.S. (1999). Determination of Copper in Edible Oils by Direct Graphite Furnace Atomic Absorption Spectrometry. *Journal of Food and Drug Analysis*, Vol.7, No.3, (June 1999), pp. 207-214, ISSN 1021-9498
- Cindric, I. J.; Zeiner, M. & Steffan, I. (2007). Trace Elemental Characterization of Edible Oils by ICP-AES and GFAAS. *Microchemical Journal*, Vol.85, (April 2006), pp. 136-139, ISSN 0026-265X
- Costa, L. M.; Silva, F. V.; Gouveia, S. T.; Nogueira, A. R. A. & Nobrega, J. A. (2001). Focused Microwave-assisted Acid Digestion of Oils: An Evaluation of the Residual Carbon Content. *Spectrochimica Acta Part B*, Vol.56, (May 2001), pp. 1981-1985, ISSN 0584-8547
- Cypriano, J.C.; Matos, M.A.C. & Matos, R.C. (2008). Ultrasound-assisted Treatment of Palm Oil Samples for the Determination of Copper and Lead by Stripping Chronopotentiometry. *Microchemical Journal*, Vol.90, (March 2008), pp. 26-30, ISSN 0026-265X
- De Leonardis, A.; Macciola, V. & DeFelice, M. (2000). Copper and Iron Determination in Edible Vegetable Oils by Graphite Furnace Atomic Absorption Spectrometry after Extraction with Diluted Nitric Acid. *International Journal of Food Science & Technology*, Vol.35, No.4, (October 1999), pp. 371-375, ISSN 0950-5423

- De Souza, R. M.; Mathias, B. M.; da Silveira, C. L. P. & Aucelio, R. Q. (2005). Inductively Coupled Plasma Optical Emission Spectrometry for Trace Multi-element Determination in Vegetable Oils, Margarine and Butter After Stabilization with Propan-1-ol and Water. *Spectrochimica Acta Part B*, Vol.60, (January 2005), pp. 711-715, ISSN 0584-8547
- Dugo, G.; La Pera, L.; La Torre, G. L. & Giuffrida, D. (2004). Determination of Cd(II), Cu(II), Pb(II), and Zn(II) Content in Commercial Vegetable Oils using Derivative Potentiometric Stripping Analysis. *Food Chemistry*, Vol.87, (December 2003), pp. 639-645, ISSN 0308-8146
- Duyck, C.; Miekeley, N.; DaSilveira, C.L.P.; Aucelio, R.Q.; Campos, R.C.; Grinberg, P. & Brandao, G.P. (2007). The Determination of Trace Elements in Crude Oil and Its Heavy Fractions by Atomic Spectrometry. *Spectrochimica Acta Part B*, Vol.62, (April 2007), pp. 939-951, ISSN 0584-8547
- Flaten, T. P. (2002). Aluminium in Tea-Concentrations, Speciation and Bioavailability. *Coordination Chemistry Reviews*, Vol.228, (February 2002), pp. 385-395, ISSN 0010-8545
- Galeano Díaz, T.; Guiberteau, A.; López Soto, M. D. & Ortiz, J. M. (2006). Determination of Copper with 5,5-dimethylcyclohexane-1,2,3-trione 1,2-dioxime 3-thiosemicarbazone in Olive Oils by Adsorptive Stripping Square Wave Voltammetry. *Food Chemistry*, Vol.96, (April 2005), pp. 156-162, ISSN 0308-8146
- Ghaedi, M.; Tavallali, H.; Shokrollahi, A.; Zahedi, M.; Montazerzohori, M. & Soylak, M. (2009). Flame Atomic Absorption Spectrometric Determination of Zinc, Nickel, Iron and Lead in Different Matrixes after Solid Phase Extraction on Sodium Dodecyl sulfate (SDS)-Coated Alumina as Their Bis (2-hydroxyacetophenone)-1,3-propanediimine chelates. *Journal of Hazardous Materials*, Vol.166, (December 2008), pp. 1441-1448, ISSN 0304-3894
- Hendrikse, P. W.; Slikkerveer, F. J.; Zaalberg, J. & Hautfenne, A. (1988). Determination of Copper, Iron and Nickel in Oils and Fats by Direct Graphite Furnace Atomic Absorption Spectrometry. *Pure and Applied Chemistry*, Vol.60, No.6, pp. 893-900, ISSN 0033-4545
- Hendrikse, P. W.; Slikkerveer, F. J.; Folkersma, A. & Dieffenbacher, A. (1991). Determination of Lead in Oils and Fats by Direct Graphite Furnace Atomic Absorption Spectrometry. *Pure and Applied Chemistry*, Vol.63, No.8, pp. 1183-1190, ISSN 0033-4545
- Huang, S.J. & Jiang, S.J. (2001). Determination of Zn, Cd and Pb in Vegetable Oil by Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry. *Journal of Analytical Atomic Spectrometry*, Vol.16, (March 2001), pp. 664-668, ISSN 0267-9477
- Hussain Reddy, K.; Prasad, N. B. L. & Sreenivasulu Reddy, T. (2003). Analytical Properties of 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone: Simultaneous Spectrophotometric Determination of Copper(II) and Nickel(II) in Edible Oils and Seeds. *Talanta*, Vol.59, (June 2002), pp. 425-433, ISSN 0039-9140

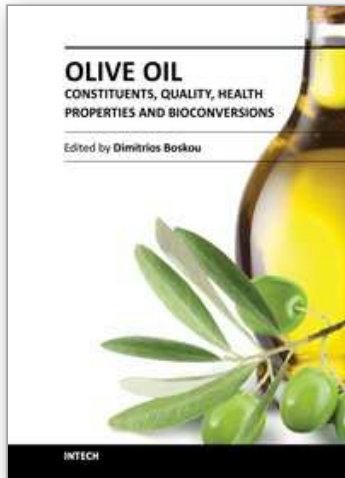
- Issa, R. M.; Khedr, A. M. & Rizk, H. F. (2005). UV-vis, IR and ^1H NMR Spectroscopic Studies of Some Schiff Bases Derivatives of 4-aminoantipyrine. *Spectrochimica Acta Part A*, Vol.62, (January 2005), pp. 621-629, ISSN 1386-1425
- İspir, E. (2009). The Synthesis, Characterization, Electrochemical Character, Catalytic and Antimicrobial Activity of Novel, Azo-containing Schiff Bases and Their Metal Complexes. *Dyes and Pigments*, Vol.82, (September 2008), pp. 13-19, ISSN 0143-7208
- Jacob, R. A. & Klevay, L. M. (1975). Determination of Trace Amounts of Copper and Zinc in Edible Fats and Oils by Acid Extraction and Atomic Absorption Spectrophotometry. *Analytical Chemistry*, Vol.47; No.4; pp. 741-743; ISSN 0003-2700
- Jimenez, M. S.; Velarte, R. & Castillo, J. R. (2003). On-line Emulsions of Olive Oil Samples and ICP-MS Multi-Elemental Determination. *Journal of Analytical Atomic Spectrometry*, Vol.18, (May 2003), pp. 1154-1162, ISSN 0267-9477
- Karadjova, I.; Zachariadis, G.; Boskou, G. & Stratis, J. (1998). Electrothermal Atomic Absorption Spectrometric Determination of Aluminium, Cadmium, Chromium, Copper, Iron, Manganese, Nickel and Lead in Olive Oil. *Journal of Analytical Atomic Spectrometry*, Vol.13, (November 1997), pp. 201-204, ISSN 0267-9477
- Khedr, A. M.; Gaber, M.; Issa, R. M. & Erten; H. (2005). Synthesis and Spectral Studies of 5-[3-(1,2,4-triazolyl-azo)-2,4-dihydroxybenzaldehyde (TA) and Its Schiff Bases with 1,3-diaminopropane (TAAP) and 1,6-diaminohexane (TAAH). Their Analytical Application for Spectrophotometric Microdetermination of Cobalt(II). Application in Some Radiochemical Studies. *Dyes and Pigments*, Vol.67, (November 2004), pp. 117-126, ISSN 0143-7208
- Khorrami, A. R.; Naeimi, H. & Fakhari, A. R. (2004). Determination of Nickel in Natural Waters by FAAS after Sorption on Octadecyl Silica Membrane Disks Modified with A Recently Synthesized Schiff's Base. *Talanta*, Vol.64, (October 2003), pp. 13-17, ISSN 0039-9140
- Kot, A. & Namiesnik, J. (2000). The role of speciation in analytical chemistry. *Trends in Analytical Chemistry*, Vol.19, Nos.2+3, pp. 69-79, ISSN 0165-9936
- Kowalewska, Z.; Bulska, E. & Hulanicki, A. (1999). Organic Palladium and Palladium-magnesium Chemical Modifiers in Direct Determination of Lead in Fractions from Distillation of Crude Oil by Electrothermal Atomic Absorption Analysis. *Spectrochimica Acta Part B*, Vol.54, (February 1999), pp. 835-843, ISSN 0584-8547
- Köse Baran, E. & Bağdat Yaşar, S. (2010). Copper and Iron Determination with [N,N'-Bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminato] in Edible Oils Without Digestion. *Journal of the American Oil Chemists Society*, Vol.87, (April 2010), pp. 1389-1395, ISSN 0003-021X
- Kurşunlu, A. N.; Guler, E.; Dumrul, H.; Kocyigit, O. & Gubbuk, I. H. (2009). Chemical Modification of Silica-gel with Synthesized New Schiff Base Derivatives and Sorption Studies of Cobalt (II) and Nickel (II). *Applied Surface Science*, Vol.255, (June 2009), pp. 8798-8803, ISSN 0169-4332
- Kurtaran, R.; Tatar Yıldırım, L.; Azaz, A. D.; Namlı, H. & Atakol, O. (2005). Synthesis, Characterization, Crystal Structure and Biological Activity of A

- Novel Heterotetranuclear Complex: $[\text{NiLPb}(\text{SCN})_2(\text{DMF})(\text{H}_2\text{O})]_2$, bis- $\{[\mu\text{-N,N'}$ -bis(salicylidene)-1,3-propanediaminato -aqua-nickel(II)] (thiocyanato) (μ -thiocyanato)($\mu\text{-N,N'}$ -dimethylformamide)lead(II)}. *Journal of Inorganic Biochemistry*, Vol.99, (May 2005), pp. 1937-1944, ISSN 0162-0134
- Lacoste, F.; Van Dalen, G. & Dysseler, P. (1999). The Determination of Cadmium in Oils and Fats by Direct Graphite Furnace Atomic Absorption Spectrometry. *Pure and Applied Chemistry*, Vol.71, No.2, pp. 361-368, ISSN 0033-4545
- Lendinez, E.; Lorenzo, M.L.; Cabrera, C. & Lopez, M.C. (2001). Chromium in Basic Foods of the Spanish Diet: Seafood, Cereals, Vegetables, Olive Oils and Dairy Products. *The Science of the Total Environment*, Vol.278, (December 2000), pp. 183-189, ISSN 0048-9697
- Levine, K.E.; Batchelor, J.D.; Rhoades, C.B. & Jones, B.T. (1999). Evaluation of a High-pressure, High-temperature Microwave Digestion System. *Journal of Analytical Atomic Spectrometry*, Vol.14, (November 1998), pp. 49-59, ISSN 0267-9477
- Li, Y.-G.; Shi, D.-H.; Zhu, H.-L.; Yan, H. & Ng, S. W. (2007). Transition Metal Complexes (M = Cu, Ni and Mn) of Schiff-Base Ligands: Syntheses, Crystal Structures, and Inhibitory Bioactivities Against Urease and Xanthine Oxidase. *Inorganica Chimica Acta*, Vol.360, (February 2007), pp. 2881-2889, ISSN 0020-1693
- List, G.R.; Evans, C.D. & Kwolek, W.F. (1971). Copper in Edible Oils: Trace Amounts Determined by Atomic Absorption Spectroscopy. *Journal of the American Oil Chemists' Society*, Vol.48, No.9, pp. 438-441, ISSN 0003-021X
- Llorent-Martinez, E. J.; Ortega-Barrales, P.; Fernandez-de Cordova, M. L.; Dominguez-Vidal A. & Ruiz-Medina, A. (2011a). Investigation by ICP-MS of Trace Element Levels in Vegetable Edible Oils Produced in Spain. *Food Chemistry*, Vol.127, (January 2011), pp. 1257-1262, ISSN 0308-8146
- Llorent-Martinez, E. J.; Ortega-Barrales, P.; Fernandez-de Cordova, M. L. & Ruiz-Medina, A. (2011b). Analysis of the Legistated Metals in Different Categories of Olive and Olive-pomace Oils. *Food Control*, Vol.22, (July 2010), pp. 221-225, ISSN 0956-7135
- Lo Coco, F.; Cecon, L.; Ciralo, L. & Novelli, V. (2003). Determination of Cadmium(II) and Zinc(II) in Olive Oils by Derivative Potentiometric Stripping Analysis. *Food Control*, Vol.14, (June 2002), pp. 55-59, ISSN 0956-7135
- Martin- Polvillo, M.; Albi, T. & Guinda A. (1994). Determination of Trace Elements in Edible Vegetable Oils by Atomic Absorption Spectrophotometry. *Journal of the American Oil Chemists Society*, Vol.71, No.4, (December 1993), pp. 347-353, ISSN 0003-021X
- Mashhadizadeh, M. H.; Pesteh, M.; Talakesh, M.; Sheikhshoaie, I.; Ardakani, M. M. & Karimi, M. A. (2008). Solid Phase Extraction of Copper (II) by Sorption on Octadecyl Silica Membrane Disk Modified with A New Schiff Base and Determination with Atomic Absorption Spectrometry. *Spectrochimica Acta Part B*, Vol.63, (March 2008), pp. 885-888, ISSN 0584-8547
- Matos Reyes, M. N. & Campos, R. C. (2006). Determination of Copper and Nickel in Vegetable Oils by Direct Sampling Graphite Furnace Atomic Absorption Spectrometry. *Talanta*, Vol.70, (May 2006), pp. 929-932, ISSN 0039-9140
- Meira, M.; Quintella, C. M.; dos Santos Tanajura, A.; da Silva, H. G. R.; Fernando, J. D. S.; da Costa Neto, P. R.; Pepe, J. M.; Santos, M. A. & Nascimento, L. L. (2011).

- Determination of the Oxidation Stability of Biodiesel and Oils by Spectrofluorimetry and Multivariate Calibration. *Talanta*, Vol.85, (April 2011), pp. 430-434, ISSN 0039-9140
- Mendil, D.; Uluözlü, Ö. D.; Tüzen, M. & Soylak, M. (2009). Investigation of the Levels of Some Element in Edible Oil Samples Produced in Turkey by Atomic Absorption Spectrometry. *Journal of Hazardous Materials*, Vol.165, (October 2008), pp. 724-728, ISSN 0304-3894
- Mohamed, G. G. (2006). Synthesis, Characterization and Biological Activity of Bis(phenylimine) Schiff Base Ligands and Their Metal Complexes. *Spectrochimica Acta Part A*, Vol.64, (May 2005), pp. 188-195, ISSN 1386-1425
- Morgan, E. (1991). *Chemometrics : Experimental Design*, John Wiley and Sons, ISBN 0 471 92903 4, Chichester, UK
- Murillo, M.; Benzo, Z.; Marcano, E.; Gomez, C.; Garaboto, A. & Marin, C. (1999). Determination of Copper, Iron and Nickel in Edible Oils using Emulsified Solutions by ICP-AES. *Journal of Analytical Atomic Spectrometry*, Vol.14, (March 1999), pp. 815-820, ISSN 0267-9477
- Nash, A. M.; Mounts, T. L. & Kwolek, W. F. (1983). Determination of Ultratrace Metals in Hydrogenated Vegetable Oils and Fats. *Journal of the American Oil Chemists Society*, Vol.60, No.4, (April 1983), pp. 811-814, ISSN 0003-021X
- Neelakantan, M. A.; Rusalraj, F.; Dharmaraja, J.; Johnsonraja, S.; Jeyakumar, T. & Sankaranarayana Pillai, M. (2008). Spectral Characterization, Cyclic Voltammetry, Morphology, Biological Activities and DNA Cleaving Studies of Amino Acid Schiff Base Metal (II) Complexes. *Spectrochimica Acta Part A*, Vol.71, (June 2008), pp. 1599-1609, ISSN 1386-1425
- Nunes, L. S.; Barbosa, J. T. P.; Fernandes, A. P.; Lemos, V. A.; dos Santos, W. N. L.; Korn, M. G. A. & Teixeira, L. S. G. (2011). Multi-element Determination of Cu, Fe, Ni and Zn Content in Vegetable Oils Samples by High-resolution Continuum Source Atomic Absorption Spectrometry and Microemulsion Sample Preparation. *Food Chemistry*, Vol.127, (December 2010), pp. 780-783, ISSN 0308-8146
- Otto, M. (1999). *Chemometrics : Statistics and Computer Application in Analytical Chemistry*, Wiley-VCH, ISBN 3-527-29628-X, Germany
- Pehlivan, E.; Arslan, G.; Gode, F.; Altun, T. & Özcan, M.M. (2008). Determination of Some Inorganic Metals in Edible Vegetable Oils by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). *Grasas y Aceites*, Vol.59, No.3, (July 2008), pp. 239-244, ISSN 0017-3495
- Pereira, J. S. F.; Moraes, D. P.; Antes, F. G.; Diehl, L. O.; Santos, M. F. P.; Guimarães, R. C. L.; Fonseca, T. C. O.; Dressler, V. L. & Flores, E. M. M. (2010). Determination of Metals and Metalloids in Light and Heavy Crude Oil by ICP-MS After Digestion by Microwave-induced Combustion. *Microchemical Journal*, Vol.96, (December 2009), pp. 4-11, ISSN 0026-265X
- Prashanthi, Y.; Kiranmai, K.; Subhashini, N. J. P. & Shivaraj. (2008). Synthesis, Potentiometric and Antimicrobial Studies on Metal Complexes of Isoxazole Schiff Bases. *Spectrochimica Acta Part A*, Vol.70, (July 2007), pp. 30-35, ISSN 1386-1425

- Rose, M.; Knaggs, M.; Owen L. & Baxter, M. (2001). A Review of Analytical Methods for Lead, Cadmium, Mercury, Arsenic and Tin Determination Used in Proficiency Testing. *Journal of Analytical Atomic Spectrometry*, Vol.16, (July 2001), pp. 1101-1106, ISSN 0267-9477
- Sant'Ana, F. W.; Santelli, R. E.; Cassella A. R. & Cassella R. J. (2007). Optimization of An Open-focused Microwave Oven Digestion Procedure for Determination of Metals in Diesel Oil by Inductively Coupled Plasma Optical Emission Spectrometry. *Journal of Hazardous Materials*, Vol.149, (March 2007), pp. 67-74, ISSN 0304-3894
- Sardans, J.; Montes, F. & Penuelas, J. (2010). Determination of As, Cd, Cu, Hg and Pb in Biological Samples by Modern Electrothermal Atomic Absorption Spectrometry. *Spectrochimica Acta Part B*, Vol.65, (November 2009), pp. 97-112, ISSN 0584-8547
- Shamspur, T.; Mashhadizadeh, M. H. & Sheikhshoae, I. (2003). Flame Atomic Absorption Spectrometric Determination of Silver Ion After Preconcentration on Octadecyl Silica Membrane Disk Modified with Bis[5-((4-nitrophenyl)azosalicylaldehyde)] As a New Schiff Base Ligand. *Journal of Analytical Atomic Spectrometry*, Vol.18, (September 2003), pp. 1407-1410, ISSN 0267-9477
- Sharaby, C. M. (2007). Synthesis, Spectroscopic, Thermal and Antimicrobial Studies of Some Novel Metal Complexes of Schiff Base Derived from [N¹-(4-methoxy-1,2,5-thiadiazol-3-yl)sulfanilamide] and 2-thiophene carboxaldehyde. *Spectrochimica Acta Part A*, Vol.66, (May 2006), pp. 1271-1278, ISSN 1386-1425
- Sikwese, F.E. & Duodu, K.G. (2007). Antioxidant Effect of A Crude Phenolic Extract from Sorghum Bran in Sunflower Oil in the Presence of Ferric Ions. *Food Chemistry*, Vol.104, (November 2006), pp. 324-331, ISSN 0308-8146
- Tantaru, G.; Dorneanu, V. & Stan, V. (2002). Schiff Bis Bases :Analytical Reagents. II : Spectrophotometric Determination of Manganese From Pharmaceutical Forms. *Journal of Pharmaceutical and Biomedical Analysis*, Vol.27, (February 2001), pp. 827-832, ISSN 0731-7085
- Templeton, D.M.; Ariese, F.; Cornelis, R.; Danielsson, L.G.; Muntau, H.; Van Leeuwen, H.P. & Lobinski, R. (2000). Guidelines for Terms Related to Chemical Speciation and Fractionation of Elements. Definitions, Structural Aspects, and Methodological Approaches. *Pure and Applied Chemistry*, Vol.72, No.8, pp. 1453-1470, ISSN 0033-4545
- Van Dalen, G. (1996). Determination of Cadmium in Edible Oils and Fats by Direct Electrothermal Atomic Absorption Spectrometry. *Journal of Analytical Atomic Spectrometry*, Vol.11, (July 1996), pp. 1087-1092, ISSN 0267-9477
- Wondimu, T.; Goessler & Irgolic, K. J. (2000). Microwave Digestion of "Residual Fuel Oil" (NIST SRM 1634b) for the Determination of Trace Elements by Inductively Coupled Plasma-Mass Spectrometry. *Fresenius Journal of Analytical Chemistry*, Vol.367, (December 1999), pp. 35-42, ISSN 0937-0633
- Yağan Aşçı, M.; Efendioğlu, A. & Batı, B. (2008). Solid Phase Extraction of Cadmium in Edible Oils using Zinc Piperazinedithiocarbamate and Its Determination by Flame Atomic Absorption Spectrometry. *Turkish Journal of Chemistry*, Vol.32, (December 2007), pp. 431-440, ISSN 1300-0527

- Zeiner, M.; Steffan, I. & Cindric, I. J. (2005). Determination of Trace Elements in Olive Oil by ICP-AES and ETA-AAS: A Pilot Study on The Geographical Characterization. *Microchemical Journal*, Vol.81, (December 2004), pp. 171-176, ISSN 0026-265X
- Ziyadanoğulları, B.; Ceviziçi, D.; Temel, H. & Ziyadanoğulları, V. (2008). Synthesis, Characterization and Structure Effects on Preconcentration and Extraction of N, N'-bis-(salicylaldehydene)-1,4-bis-(p-aminophenoxy) butane towards Some Divalent Cations. *Journal of Hazardous Materials*, Vol.150, (April 2007), pp. 285-289, ISSN 0304-3894



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