

Copper and Iron Determination with [*N,N'*-Bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminato] in Edible Oils Without Digestion

Eda Köse Baran · Sema Bağdat Yaşar

Received: 3 December 2009 / Revised: 4 April 2010 / Accepted: 24 April 2010 / Published online: 18 September 2010
© AOCS 2010

Abstract A new method for the determination of copper(II) and iron(III) in liquid edible oils which does not require a digestion step was developed. The suggested method involves extraction of metals with [*N,N'*-bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminato] (LDM) followed by flame atomic absorption spectrometry measurement. As a first step, metal complexes of copper(II) and iron(III) ions with LDM were investigated spectrophotometrically. After the analytical properties and experimental conditions of the complexation had been determined, these findings were used to determine the extraction period as a second step. Experimental conditions were optimized using a central composite design. Optimum conditions for Cu(II) and Fe(III) extractions from oil were found: the ratios of the volume of Schiff base solution used to the mass of oil ($V_{\text{LDM}}/m_{\text{oil}}$; mL g⁻¹) were 0.76 and 1.19 mL g⁻¹, the stirring times were 73 and 67 min, and the temperatures were 31 and 28 °C, respectively. The developed extraction and determination method was tested on certified reference materials; the recovery percentages were found to be 99.4 ± 2.8 and 100.2 ± 5.6 for Cu(II) and Fe(III), respectively. The suggested method was performed on real samples such as olive oil, sunflower oil, corn oil, canola oil and recovery values between 97.2–102.1 for Cu(II) and 94.5–98.6 for Fe(III) were determined. It was concluded that the developed method has some advantages over the common traditional method

including rapidity, sensitivity, accuracy, reduced risk and cost.

Keywords Edible oil · Iron · Copper · [*N,N'*-bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminato] · Schiff base · Flame atomic absorption spectrometry

Introduction

Olive oil and its components have well known nutritional benefits. It is widely known that some metals such as Cu, Fe, Zn, Ni, Cr, Co and Mn catalyze oxidation, and even at low levels of concentration, cause rancidity in olive oil. The formations of peroxides, aldehydes, ketones and other components may occur as the results of these oxidation reactions. Therein lies the importance of the determination of metals in olive oil.

Most techniques for the determination of metals in edible oils require sample pretreatment. According to the literature, microwave digestion of oils for the determination of some metals is widely used with highly sensitive instruments such as ICP-OES or ICP-MS [1–5]. Additionally, preconcentration techniques appropriate for the analyte may be required with a digestion procedure, making the whole procedure time consuming. When dry ashing is used as the method of digestion for edible oils, sample dilution is minimized more than microwave digestion, the risk of contamination is too high and precision is not as good [6]. Extraction with acids can also be used for analyzing metals in olive oil. It's disadvantage is that the precision of the extraction efficiency is not as good. When ET-AAS or ICP are used for the determination of metals in edible oils, a rapid pretreatment is possible by dilution with organic solvents such as methyl isobutyl ketone (MIBK).

E. K. Baran
Institute of Science and Technology,
Balıkesir University, Çağış, 10145 Balıkesir, Turkey

S. B. Yaşar (✉)
Chemistry Department, Faculty of Science and Arts,
Balıkesir University, Çağış, 10145 Balıkesir, Turkey
e-mail: sbyasar@balikesir.edu.tr

However, plasma stability and detection limits are not as good as when aqueous solutions are used [7–12].

Schiff bases, which have good metal complexing capabilities, have been used as ligands in metal complexes for recent analytical applications [13–22]. The use of Schiff bases as a radiological material, liquid crystal material or analytical separator has been documented [23, 24]. An interesting attribute of Schiff bases and their complexes is their antimicrobial and antifungal activity [25, 26].

In the present work, a simple, cheap, rapid, sensitive and accurate method for the determination of iron and copper in liquid edible oil was developed. Iron and copper in oil samples were extracted from the oil phase to the aqueous phase without digestion, using [*N,N'*-bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminato] as a Schiff base ligand. The Schiff-base ligand used in the present work is shown in Fig. 1.

To optimize the conditions for metal extraction from oils, namely the ratio of Schiff base/olive oil, stirring time and temperature by a central composite design method was employed. The developed extraction technique for the determination of copper and iron in liquid edible oils can be used as a more efficient, cheap, rapid, sensitive and accurate method as compared to conventional methods in which time consuming digestion or metal extraction steps are involved.

Materials and Methods

Chemicals

A Merck Titrisol 109972 iron stock solution (1,000 mg iron in mL; FeCl₃ in 15% HCl) and copper stock solution (1,000 mg copper in mL; CuCl₂·2H₂O Merck) were used for preparing the standard solutions. Conostan iron standard (5,000 μg g⁻¹; code number: 354770) and Conostan copper standard (5,000 μg g⁻¹; code number: 687850) were used as certified reference materials (CRM) for optimization of experimental conditions and testing the improved method. [*N,N'*-bis(salicylidene)-2,2'-dimethyl-

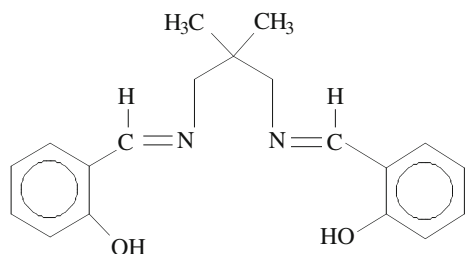


Fig. 1 The molecular structure of [*N,N'*-bis(salicylidene)-2,2'-dimethyl-1,3-propanediaminato] [27]

1,3-propanediaminato] (LDM) was synthesized and the structure of this Schiff base was clarified by Kurtaran et al. [27]. Stock solution of Schiff base was prepared by dissolving 0.1552 g LDM in 100 ml of 88% (v/v) ethanol–water. Appropriate amounts of stock solution were used for the preparation of the standard Schiff base solution (1×10^{-3} mol L⁻¹). Stock and standard solutions of LDM were kept in polyethylene containers to protect them from the light and temperature.

HCl (Merck) and NaOH (Merck) for pH 1, 2, 3; sodium acetate/acetic acid (Riedel-de Haen) for pH 4, 5; tris(hydroxymethyl)aminomethane (Merck) for pH, 6, 7; ammonia/ammonium nitrate (Merck) for pH 8, 9, 10, 11 and 12 were used to adjust the pH of the medium. All the reagents were analytical grade and doubly distilled water was used throughout.

Apparatus

A Varian Cary 1E UV–Vis spectrophotometer with 1.0-cm quartz cells was used to study the spectral properties of ligand and metal–ligand complexes. Copper and iron determinations in extracts were made by using a Unicam 929 A flame atomic absorption spectrometer (FAAS) equipped with deuterium background correction. The hollow cathode lamps for iron and copper were manufactured by the Koto Electric Co. Ltd and Unicam Analytic Systems, respectively. The FAAS operation conditions found to be convenient for each metal are given in Table 1. A Nel pH meter, Nüve heating bath and Heidolph magnetic stirrer were also used.

Procedures

All the spectral studies were performed in 88% (v/v) ethanol–water. The solutions of ligand, metal and complex used in the experiments were incubated at 25 °C. The absorption spectra of Schiff base, metal and a mixture of Schiff base with metal ions (Cu(II) and Fe(III)) were analyzed in order to reveal the most appropriate wavelengths. Figure 2 shows the absorption spectra of the solutions of 1×10^{-3} mol L⁻¹ for the ligand and the complexes of each metal. As can be seen from Fig. 2,

Table 1 Operation conditions for iron and copper in FAAS

| Parameters | Cu | Fe |
|---------------------------------------|-------|-------|
| Wavelength (nm) | 324.8 | 248.3 |
| Spectral band width (nm) | 0.5 | 0.2 |
| Lamp Current (mA) | 3.5 | 5.0 |
| Fuel flow rate (L min ⁻¹) | 0.70 | 0.70 |
| Flame height (mm) | 13 | 13 |

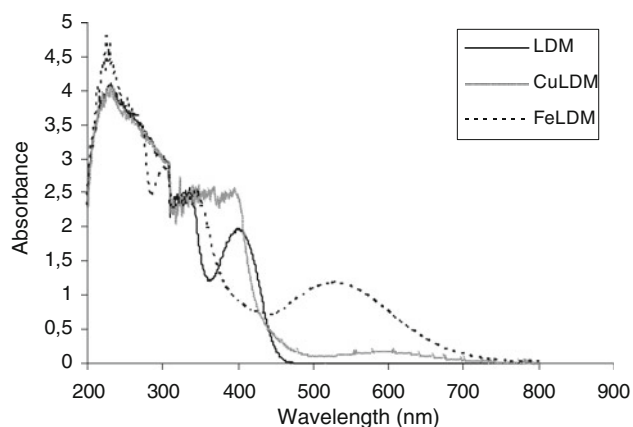


Fig. 2 The absorption spectra of LDM and complexes (Cu-LDM; Fe-LDM)

the most appropriate wavelengths of the complexes are 363 nm for Cu and 529 nm for Fe.

Kinetic studies were carried out to observe the period of the formation of metal complexes. The absorbances of the solutions prepared by mixing a solution of 1×10^{-3} mol L⁻¹ ligand with that of 1×10^{-3} mol L⁻¹ metal ions were recorded for 60 min. Five minutes was determined to be the time required to obtain a constant absorbance. In that process, experiments were performed at 363 and 529 nm for Cu and Fe, respectively.

The absorbance of metal complexes at different pH values was measured against the reagent blank with a UV-Vis spectrophotometer at their selected wavelengths. The ratio of the buffer solution volume to the final solution volume was 1:10 and the same amounts of buffer solutions were added for each solution used in the studies for the adjustment of pH.

Optimization of Experimental Conditions

To determine the optimum conditions in the procedure of extracting metals from oil phase to aqueous phase, central composite design was applied [28, 29]. Factors influencing the extraction efficiency of metals studied in the present work were the ratio of the volume of the Schiff base solution used to the amount of oil ($V_{\text{LDM}}/m_{\text{oil}}$; mL g⁻¹), the stirring time and the temperature. Ranges determined were 0.5–1.5 mL g⁻¹; 30–90 min; 20–40 °C for the first, second and third factors, respectively. Table 2 shows the factors, the levels and their values.

In this study, 20 experiments were carried out to the extent of the Central Composite Design. Analytes (Cu(II), Fe(III)) concentrations in CRMs were 20 mg kg⁻¹. The metal contents of the extracts obtained from each experiment were determined by FAAS using the standard addition calibration method. The absorbance values obtained with FAAS were used to establish recovery values for the

Table 2 Levels and the values of levels used in Central Composite Design

| Levels | -1.682 | -1 | 0 | +1 | +1.682 |
|---|--------|-----|----|-----|--------|
| X_1 (1st factor) | | | | | |
| $V_{\text{LDM}}/m_{\text{oil}}$ ratio (mL g ⁻¹) | 0.159 | 0.5 | 1 | 1.5 | 1.841 |
| X_2 (2nd factor) | | | | | |
| Stirring time (min) | 9.56 | 30 | 60 | 90 | 110.46 |
| X_3 (3rd factor) | | | | | |
| Temperature (°C) | 13.18 | 20 | 30 | 40 | 46.82 |

extraction of metals from oil. The calculated values of $1/(100 - \text{Recovery } \%)$ were considered as response values (y) in Central Composite Design procedure. A mathematical matrix (X) was established for the determination of the parameters to be changed for each experiment.

b Values were calculated by applying to the X matrix. y equations (Eqs. 1 and 5 for Cu(II) and Fe(III), respectively) were constructed based on the b values. The values for X_1 , X_2 and X_3 which makes the y equations zero were calculated as optimum conditions.

Application of the Method

The improved present method was applied to some liquid edible oils under the optimum experimental conditions. Certain levels of CRM were added to the oil samples, and the final concentration of the added metal standards was adjusted to 20 mg kg⁻¹. The oil sample and Schiff base (in ethanol/water) solutions were mixed at optimum $V_{\text{LDM}}/m_{\text{oil}}$ ratio and stirred under the optimum conditions. The ethanol/water phase including the metal-LDM complex was separated and then the concentrations of Cu(II) and Fe(III) were determined by FAAS.

Results and Discussion

From the absorption spectra of LDM, Cu-LDM and Fe-LDM at pH 4.0 in Fig. 2, the maximum absorbance values were observed at 401, 363 and 529 nm, respectively. The composition of complexes of both metal ions was determined by a continuous variation method. Job's plot for copper and iron complexes confirmed a 1:1 (Metal:LDM) composition for both of the complexes. Absorption measurements were performed 5 min after the mixing reagent as determined by the equilibrium time experiments.

The Effect of pH on the Complexes

Adjustment of pH is necessary for the determination of the complexation ratio of the Schiff base and the metals.

Owing to the destruction of the structures of complexes at pHs <2 and the existence of the possibility of saponification of oil and precipitation of metal hydroxides at pHs >7, the pH range of 2–8 was evaluated to determine the optimum pH for complexation. According to the results obtained, pH 4 was chosen to be the optimum (Fig. 3).

The Optimization of Conditions for Metal Extraction from Oils

Experimental conditions for the suggested method in this work should be optimized in order to get the most efficient results. Results appearing in Table 3 were used in the central composite design. To the given amount of oil samples containing 20.0 mg L⁻¹ Cu(II) or Fe(III) standards, a certain volume of 1 × 10⁻³ M LDM solution was added. After stirring for the desired period of time at the optimum temperature, the aqueous phase was separated and its metal concentration was determined by FAAS. The optimization of V_{LDM}/m_{oil} ratio, stirring time and temperature was carried out at the conditions corresponding to code values given in Table 2.

By using the data in Table 3 in the central composite design standard procedure [28, 29], a *y* equation was obtained for Cu(II) as following:

$$y = 0.074479x_1 - 0.09842x_2 - 0.00327x_3 + 0.0065x_1^2 + 0.027201x_2^2 + 0.251628x_3^2 - 0.15978x_1x_2 + 0.080751x_1x_3 - 0.07861x_2x_3 - 0.1646x_1x_2x_3 \quad (1)$$

By equalization of the derivatives of Eq. 1 in terms of X₁, X₂, X₃ to zero, respectively, we obtain Eqs. 2–4.

$$\frac{dy}{dx_1} = 0.074479 + 0.013x_1 - 0.15978x_2 + 0.080751x_3 - 0.1646x_2x_3 = 0 \quad (2)$$

$$\frac{dy}{dx_2} = -0.09842 + 0.054402x_2 - 0.15978x_1 - 0.07861x_3 - 0.1646x_1x_3 = 0 \quad (3)$$

$$\frac{dy}{dx_3} = -0.00327 + 0.503256x_3 + 0.080751x_1 - 0.07861x_2 - 0.1646x_1x_2 = 0 \quad (4)$$

Similarly, the *y* equation was obtained for Fe(III) by using the data in Table 3 in the central composite design standard procedure. The constructed *y* Eq. 5 is given as the following:

$$y = -0.04406x_1 + 0.052283x_2 + 0.210066x_3 + 0.086966x_1^2 + 0.089654x_2^2 + 0.250638x_3^2 - 0.33978x_1x_2 - 0.17359x_1x_3 + 0.030373x_2x_3 - 0.47376x_1x_2x_3 \quad (5)$$

Equalization of the derivatives of Eq. 5 in terms of X₁, X₂, X₃ to zero, respectively, gave Eqs. 6–8 for Fe(III).

$$\frac{dy}{dx_1} = -0.04406 + 0.173932x_1 - 0.33978x_2 - 0.17359x_3 - 0.47376x_2x_3 = 0 \quad (6)$$

$$\frac{dy}{dx_2} = 0.052283 + 0.179308x_2 - 0.33978x_1 + 0.030373x_3 - 0.47376x_1x_3 = 0 \quad (7)$$

Fig. 3 The effect of pH on the complexes

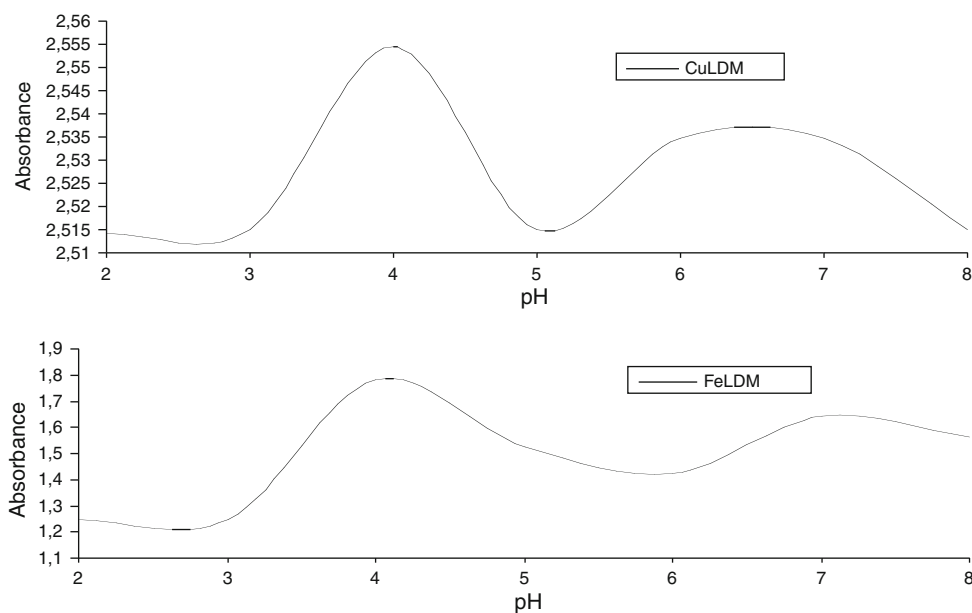


Table 3 Recovery and response values for the extraction of Cu(II) and Fe(III) from olive oil

| Experiment | X_1 V_{LDM}/m_{oil} (mL g ⁻¹) | X_2 Time (min) | X_3 Temp (°C) | Cu(II) | | Fe(III) | |
|------------|--|------------------|-----------------|--------|----------|---------|----------|
| | | | | Rec % | Response | Rec % | Response |
| 1 | 1/2 | 30 | 20 | 103.4 | 0.296 | 101.2 | 0.801 |
| 2 | 1.5 | 30 | 20 | 101.6 | 0.625 | 82.3 | 0.056 |
| 3 | 1/2 | 90 | 20 | 104.7 | 0.211 | 93.0 | 0.166 |
| 4 | 1.5 | 90 | 20 | 103.6 | 0.282 | 87.6 | 0.080 |
| 5 | 1/2 | 30 | 40 | 76.8 | 0.043 | 67.5 | 0.031 |
| 6 | 1.5 | 30 | 40 | 107.5 | 0.133 | 102.1 | 0.481 |
| 7 | 1/2 | 90 | 40 | 111.8 | 0.085 | 103.6 | 0.274 |
| 8 | 1.5 | 90 | 40 | 100.9 | 1.136 | 99.3 | 1.389 |
| 9 | 1 | 60 | 30 | 96.2 | 0.260 | 99.5 | 2.155 |
| 10 | 0.159 | 60 | 30 | 31.8 | 0.015 | 36.7 | 0.016 |
| 11 | 1.841 | 60 | 30 | 108.8 | 0.113 | 107.3 | 0.137 |
| 12 | 1 | 9.56 | 30 | 58.4 | 0.024 | 52.6 | 0.021 |
| 13 | 1 | 110.46 | 30 | 118.4 | 0.054 | 117.9 | 0.056 |
| 14 | 1 | 60 | 13.18 | 91.8 | 0.122 | 84.3 | 0.064 |
| 15 | 1 | 60 | 46.82 | 86.4 | 0.074 | 65.1 | 0.029 |
| 16 | 1 | 60 | 30 | 98.0 | 0.992 | 98.2 | 0.563 |
| 17 | 1 | 60 | 30 | 97.9 | 0.473 | 97.7 | 0.440 |
| 18 | 1 | 60 | 30 | 100.3 | 3.906 | 97.9 | 0.473 |
| 19 | 1 | 60 | 30 | 101.3 | 0.762 | 96.2 | 0.266 |
| 20 | 1 | 60 | 30 | 99.4 | 1.602 | 99.3 | 1.389 |

$$\frac{dy}{dx_3} = 0.210066 + 0.501276x_3 - 0.17359x_1 + 0.030373x_2 - 0.47376x_1x_2 = 0 \tag{8}$$

Equations 2–4 for Cu and 6–8 for Fe were solved using Derive 6 computer software and code values of X_1 , X_2 and X_3 were obtained. These code values were transformed to the true values providing the optimum conditions of the factors. The results are given in Table 4.

Application of the Improved Extraction Method to the Certified Reference Materials

The extraction procedure has been applied to the CRMs under the optimum experimental conditions given in Table 4. As seen in Table 5, the recovery percentages are satisfactory enough to extract and determine Fe(III) and Cu(II) in oil without any digestion or extraction steps. LDM is suggested for the extraction of Cu(II) and Fe(III) from liquid edible oils as an appropriate ligand under the optimum experimental conditions.

The limit of detection (LOD) of the suggested method for Fe and Cu was found to be 6.0 and 2.0 mg kg⁻¹ respectively. The recovery percentages 99.4 (±2.8) and 100.2 (±5.6) obtained by application of the method to CRMs show that the suggested method is very suitable for liquid edible oils for the determination of Cu(II) and Fe(III).

Table 4 Optimum extraction conditions for Cu(II) and Fe(III) by LDM

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

Application of Real Samples

To test the applicability of the developed procedure, it was applied to the extraction and determination of Cu(II) and Fe(III) content from different edible oil samples by FAAS. Oil samples were collected from Turkish markets. As can be seen from Table 6, the results for real oil samples were acceptable.

Study of Interferences

The effects of foreign metal ions on the extraction of Cu(II) and Fe(III) ions from oil to the aqueous phase were investigated by measuring the absorbance of solutions containing 3 mg L⁻¹ analyte in the presence of foreign ions in the range of 3–3,000 mg L⁻¹. Tolerance limits of foreign ions were taken as that value which caused an error of not more than ±5% in the absorbance differences. The

Table 5 Recovery values for the extraction of Cu(II) and Fe(III) from oil (CRM) under the optimum experimental conditions ($n = 10$)

| CRM | Certified value ($\mu\text{g g}^{-1}$) | Founded value ($\mu\text{g g}^{-1}$) | Mean recovery (%) | Standard deviation |
|------------------------------------|--|--|-------------------|--------------------|
| Conostan 687850 (Cu(II) standard) | 25.9 | 25.7 | 99.4 | 2.8 |
| Conostan 354770 (Fe(III) standard) | 26.1 | 26.1 | 100.2 | 5.6 |

Table 6 Recovery values for the extraction of Cu(II) and Fe(III) from various oil samples

| Samples | Certified value ($\mu\text{g g}^{-1}$) | Value found ($\mu\text{g g}^{-1}$) | Mean recovery (%) | Standard deviation |
|---------------|--|--------------------------------------|-------------------|--------------------|
| Olive oil | | | | |
| Cu | 20.0 | 19.9 ± 0.2 | 99.8 | 1.2 |
| Fe | 20.0 | 19.7 ± 0.2 | 98.6 | 0.8 |
| Sunflower oil | | | | |
| Cu | 20.0 | 19.4 ± 0.2 | 97.2 | 0.8 |
| Fe | 20.0 | 18.9 ± 0.2 | 94.5 | 0.8 |
| Corn oil | | | | |
| Cu | 20.0 | 20.4 ± 0.3 | 102.1 | 1.3 |
| Fe | 20.0 | 19.3 ± 0.3 | 96.7 | 1.7 |
| Canola oil | | | | |
| Cu | 20.0 | 19.5 ± 0.2 | 97.7 | 0.7 |
| Fe | 20.0 | 19.0 ± 0.3 | 95.2 | 1.5 |

tolerance limits for Na, Mn and Zn on 3 mg kg^{-1} Cu(II) solutions were 150, 1,500 and 30 mg kg^{-1} , respectively. The tolerance limit for Cu on 3 mg kg^{-1} Fe(III) was 150 mg kg^{-1} .

Conclusion

In the present work, a simple extraction procedure without digestion was developed for the determination of Cu and Fe in liquid edible oils. Cu and Fe concentrations of liquid edible oils were determined by FAAS after the extraction of both metals with LDM into the aqueous phase. The metal determination methods in oils require sensitive instruments such as ICP-OES and GF-AAS, are expensive and also require an acid digestion or extraction step which have some disadvantages such as risk of explosion or contamination as well as being time consuming, etc. The suggested determination strategy after the extraction step with LDM were found to have some advantages: (1) no need to use expensive instruments, i.e. ICP-OES or GF-AAS, (2) protection from some interferences caused by highly organic matrices of oil, (3) greatly reduced explosion risk during decomposition, (4) high recovery and sensitivity values, and also (5) rapid and cheap.

Acknowledgments The authors would like to thank the Research and Application Center for Environmental Concern of Balıkesir University. Dr. Mahir Alkan and Dr. Raif Kurtaran are also gratefully acknowledged. This study was supported by the Scientific and Technological Research Council of Turkey (Tübitak-TBAG project number: 105T153).

References

1. Bağdat Yaşar S, Güçer Ş (2004) Fractionation analysis of magnesium in olive products by atomic absorption spectrometry. *Anal Chim Acta* 505:43–49
2. Costa LM, Silva FV, Gouveia ST, Nogueira ARA, Nobrega JA (2001) Focused microwave-assisted acid digestion of oils: an evaluation of the residual carbon content. *Spec Chim Acta B* 56:1981–1985
3. Wondimu T, Goessler W, Irgolic KJ (2000) Microwave digestion of “residual fuel oil” (NIST SRM 1634b) for the determination of trace elements by inductively coupled plasma-mass spectrometry. *J Anal Chem* 367:35–42
4. Bettinelli M, Spezia S, Baroni U, Bizzarri 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. *J Anal At Spectrom* 10:555–560
5. Levine KE, Batchelor JD, Rhoades CB, Jones J, Jones BT (1999) Evaluation of a high-pressure, high-temperature microwave digestion system. *J Anal At Spectrom* 14:49–59
6. Carbonell V, Mauri AR, Salvador A, Guardia M (1991) Direct determination of copper and iron in edible oils using flow injection flame atomic absorption spectrometry. *J Anal At Spec* 6:581–584
7. Slikkerveer FJ, Braad AA, Hendrikse PW (1980) Determination of phosphorus in edible oils by graphite furnace atomic absorption spectroscopy. *At Spectrosc* 1:30–32
8. 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. *At Spectrosc* 9:107–109
9. Castillo JR, Jimenez MS, Ebdon L (1999) Simultaneous determination of metals in olive oil using direct emulsion nebulization. *J Anal At Spectrom* 14:1515–1518
10. Dalen VG (1996) Determination of cadmium in edible oils and fats by direct electrothermal atomic absorption spectrometry. *J Anal At Spectrom* 11:1087–1092
11. Guillaumin R (1966) Determination of calcium and magnesium in vegetable oils and fats by atomic absorption spectrophotometry. *At Absorpt Newsl* 5:19–21
12. Lelievre C, Hennequin D, Lequerler JF, Barillier D (2000) A rapid method for the direct determination of copper and iron in butter by GFAAS. *At Spectrosc* 21:23–29
13. Afkhami A, Tarighat MA, Khanmohammadi H (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* 77:995–1001
14. Ashkenani H, Dadfarnia S, Shabani AMH, Jaffari AA, 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. *J Hazard Mater* 161:276–280
15. Ghaedi M, Tavallali H, Shokrollahi A, Zahedi M, Montazer-zohori 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. *J Hazard Mater* 166:1441–1448
 16. Ghaedi M, Shabani R, Shokrollahi A, Montazer-zohori M, Sahr-aeian A, Soylak M (2009) Preconcentration and separation of trace amounts of copper (II) on N^1, N^2 -bis(4-fluorobenzylidene)ethane-1,2-diamine loaded on Sepabeads SP70. *J Hazard Mater* 170:169–174
 17. Kursunlu AN, Guler E, Dumrul H, Kocyigit O, Gubbuk IH (2009) Chemical modification of silica-gel with synthesized new Schiff base derivatives and sorption studies of Cobalt (II) and Nickel (II). *Appl Surf Sci* 255:8798–8803
 18. Ziyadanoğulları B, Ceviziçi D, Temel H, Ziyadanoğulları R (2008) Synthesis, characterization and structure effects on pre-concentration and extraction of N, N' -bis(salicylaldehyde)-1,4-bis-(*p*-aminophenoxy) butane towards some divalent cations. *J Hazard Mater* 150:285–289
 19. Tantar G, Dorneanu V, Stan M (2002) Schiff bis bases: analytical reagents. II: spectrophotometric determination of manganese from pharmaceutical forms. *J Pharm Biomed Anal* 27:827–832
 20. Mashaly M, Bayoumi HA, Taha A (1999) Metal complexes of triazine Schiff bases spectroscopic and thermodynamic studies of complexation of some divalent metal ions with 3-[2-(1-acetyl-ethylidene)hydrazino]-5,6-diphenyl-1,2,4-triazine. *Chem Papers* 53:299–308
 21. Shamspur T, Mashhadizadeh MH, Sheikhsheoie 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. *J Anal At Spectrom* 18:1407–1410
 22. Khedr AM, Gaber M, Issa RM, 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 Pigment* 67:117–126
 23. Reichert DE, Lewis JS, Anderson CJ (1999) Metal complexes as diagnostic tools. *Coord Chem Rev* 184:3–66
 24. Hoshino H, Saitoh Y, Nakano K, Takahashi T, Yotsuyanagi T (2001) Reversed-phase high-performance liquid-chromatographic determination system specific to ultratrace hard metal ions with tridentate Schiff bases. *Bull Chem Soc Jpn* 74:1279–1284
 25. Chandra S, Gupta LK (2005) Modern spectroscopic techniques in the characterization of schiff base macrocyclic ligand and its complexes with transition metals. *Spec Chim Acta A* 62:307–312
 26. Neelakantan MA, 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. *Spec Chim Acta A* 71:1599–1609
 27. Arıcı C, Ercan F, Kurtaran R, Atakol O (2001) [N, N' -Bis(salicylidene)-2,2-dimethyl-1,3-propanediaminato] nickel(II) and [N, N' -bis(salicylidene)-2,2-dimethyl-1,3-propanediaminato] copper(II). *Acta Crystallogr C* 57:812–814
 28. Otto M (1999) *Chemometrics: statistics and computer application in analytical chemistry*. Wiley, Germany
 29. Morgan E (1991) *Chemometrics: experimental design*. Wiley, London