Food Chemistry 197 (2016) 445–449

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Extraction of nickel from edible oils with a complexing agent prior to determination by FAAS

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ARTICLE INFO

Article history:
Received 19 March 2014
Received in revised form 3 October 2015
Accepted 1 November 2015
Available online 2 November 2015

Keywords:
Edible oils
Nickel
N,N′-bis(4-methoxysalicylidene) ethylenediamine
Schiff base
Central composite design
Flame atomic absorption spectrometry

ABSTRACT

In the present work, a new extraction method for separation of nickel from edible oils and determination by FAAS is reported. This method is based on extraction of Ni(II) ions from the oil to aqueous phase with N,N′-bis(4-methoxysalicylidene) ethylenediamine (MSE) and determination by FAAS. Properties of the complex formed between MSE and Ni(II) were investigated spectrophotometrically. Central composite design (CCD) was utilized for optimization of MSE to oil, stirring time and temperature, which were 0.97 mL g^{-1}, 15.4 min, and 29.7 °C, respectively. The developed method was tested with an oil-based metal standard and the recovery was 93.8 ± 3.9%. The proposed method was applied with five different edible oils.

1. Introduction

Oils are a key component of the human diet and have important roles in biological reactions. Plant-derived edible oils are commonly used in cooking as well as cosmetics and pharmaceuticals. Trace metal concentration is an important criterion for the quality and shelf life of oils. It is known that trace levels of Cu, Fe, Zn, Ni, Cr, Mn and Co catalyze oxidation reaction and might produce peroxides, aldehydes and ketones. These compounds affect the color, taste and odor of oils. Consequently, information about the concentrations of these trace metal ions is very useful (Afkhami, Abbasi-Tarighata, & Khanmohammadi, 2009; Bakırcıoğlu, Topraksever, & Kurtulus, 2014; Reyes & Campos, 2006).

According to the literature, various techniques, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) (Anthemidis, Arvanitidis, & Stratis, 2005; de Souza, Mathias, da Silveira, & Aucelio, 2005), mass spectrometry (ICP-MSE) (Martinez, Barrales, Cordova, Vidal, & Medina, 2011), flame atomic absorption spectrometry (FAAS) (Baran & Yaşar, 2010; Nunes et al., 2011; Yağan Aşcı, Efendioğlu, & Batı, 2008), potentiometric and voltammetric (Diaz, Guiberteau, Soto, & Ortiz, 2006; Dugo, Pera, Torre, & Giuffrida, 2004) techniques, have been used for metal determination in oil. In these techniques, eliminating the organic matrix requires wet digestion, dry ashing, microwave-assisted acid digestion, acid extraction and solid phase extraction (SPE). However, this pre-processing is time consuming, taking several hours to be completed, can cause contamination or loss of elements, and there is a risk of explosion. Furthermore, the accuracy and precision of result obtained can also be unsatisfactory. Electrothermal atomic absorption spectrometry (ETAAS) (Cindric, Zeiner, & Steffan, 2007; Reyes & Campos, 2006) and neutron activation analysis (NAA) (Obi, Jonah, & Umar, 2001) have been used to analyze edible oils without any pre-treatment. However, widespread use is not possible due to costs.

In recent years, complexing agents have had a more important role and been used widely in analytical applications. Due to the high complexation capacity of ligands, they have been utilized in sample preparation for separation or pre-concentration of metal ions prior to detection. In numerous reports, ligands such as N,N′-bis(3-methylsalicylidene)-ortho-phenylene diamine (Fakhari, Khorrami, & Naeimi, 2005), ammonium pyrrolidine dithiocarbamate (Jalbani & Soylak, 2015), dimethylglyoxime (Sancho, Deban, Campos, Pardo, & Vega, 2000), di-(2-ethyl hexyl phosphoric acid) (Vellaichamy & Palanivelu, 2011), p-nitrophenylazoresorcinol (Şahin, Efeçınar, & Şatıroğlu, 2010), 4-(2-pyridylazo)-resorcinol (Silva, Roldan, & Gine, 2009), 1-(2-Pyridylazo)-2-naphthol (Bidabadi, Dadfarnia, & Shabani, 2009) and N,N′-ethylenebis (ethane sulfonamide) (Karacan & Aslantaş, 2008), have been used

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http://dx.doi.org/10.1016/j.foodchem.2015.11.001
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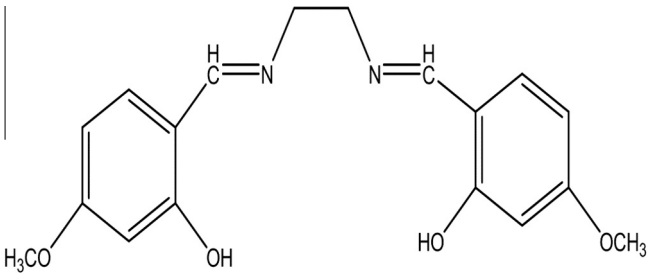

Fig. 1. Molecular structure of N,N′-bis(4-methoxysalicylidene) ethylenediamine (MSE).

for separation or pre-concentration of nickel and the other trace metals in food samples.

Liquid–liquid extraction (LLE) is one of the most useful technique for the isolation of analytes from interfering matrices or pre-concentration of analyte from larger volumes. LLE is based on distribution of the analyte between two immiscible solvents, one of which is usually water (aqueous phase) and the other an organic solvent (organic phase). Use of chelating agents, which contain sulfur, nitrogen and/or oxygen groups, increases the extraction of analytes (Anthemidis & Ioannou, 2009; Silvestre, Santos, Lima, & Zagotta, 2009). A literature survey reveals that LLE has been used for separation or pre-concentration of organic and inorganic analyte(s) from various food samples (Alshana, Ertaş, & Göğer, 2015; Jalbani & Soylak, 2015; Khajeh, 2011; Peng et al., 2015; Shrivas & Jaiswal, 2013). Considering the bottleneck in sample preparation step of oils, LLE provides an opportunity for simple, cheap, accurate and sensitive determination of Ni(II) in edible oils.

In the present work, a Schiff base, N,N′-bis (4-methoxysalicylidene) ethylenediamine (MSE, shown in Fig. 1) was used as an complexing agent for the extraction of Ni(II) ion from edible oil. To complete complexation, ethanolic aqueous solution of MSE and oil sample were mixed, and convenient extraction conditions assigned. The ratio of MSE to oil, stirring time and temperature parameters were optimized and modeled using central composite design (CCD) procedure and response surface methodology (RSM).

2. Material and methods

2.1. Statistical software

Design Expert 8.0 was used to design experiments, and model and analyze the results. Equations obtained from CCD were solved using Microsoft® Excel.

2.2. Reagents

All chemicals used were analytical reagent grade. Water, used throughout the experiments and to prepare all of the solutions, was purified by reverse osmosis. All containers and glassware were soaked in 10% nitric acid for at least 24 h and rinsed three times with water before use.

Merck Titrisol 109989 stock nickel standard (1000 mg nickel L^{-1}; $NiCl_2$ in H_2O) (Darmstadt, Germany) was used for preparation of standard solutions. Conostan oil-based nickel standard (5000 mg kg^{-1}, catalog number: 506516) (Baie D'Urfe, Canada) was used for optimization by diluting it in n-hexane, (Darmstadt, Germany) and to spike the real samples for testing the improved method. N,N′-bis(4-methoxysalicylidene) ethylenediamine (MSE) was synthesized as described before using a condensation reaction with 4-methoxysalicylidene and diamino ethane (Darmstadt, Germany) (Tokay & Yaşar, 2011). MSE stock solutions were prepared by dissolving the ligand in 85% ethanol (Merck)-water mixture (1×10^{-3} mol L^{-1}). In the interference study, cations were added as nitrate salts (Merck, Darmstadt, Germany). The oil samples were purchased from local vendors and stored in original packages at room temperature.

2.3. Apparatus

Spectra of the ligand and nickel complex were monitored using PG instruments Ltd. T80+ UV–Vis spectrophotometer (Leicestershire, UK). Determination of nickel in aqueous ethanolic solutions was carried out using a Perkin Elmer AAnalyst200 FAAS (Waltham, MA, USA) equipped with deuterium background correction. Multi element Lumina hollow cathode lamp was used as line source. Instrumental operating parameters were adjusted according to the manufacturers' instructions, unless otherwise specified. A Thermo Orion 5 Star model pH meter (Waltham, MA, USA) was used for pH measurements and a Heidolph MR 3001 K model magnetic stirrer (Schwabach, Germany) was employed during the extraction procedure. CEM Mars 5 microwave digestion system (Matthews, NC, USA) and Perkin Elmer Optima 3100 XL ICP-OES (Waltham, MA, USA) were used for the conventional method.

2.4. Proposed analytical procedure

The spectral studies and investigation of MSE and its nickel complex were carried out in 85% (v/v) ethanol–water mixture at 1×10^{-5} mol L^{-1}. Kinetic studies were performed at 278 nm with 10 s intervals for 60 min to determine the period needed to achieve equilibrium. The effect of pH was also evaluated within the range 2–10. Adjustment of pH was performed by adding 1 mL buffer solution at a given pH to the MSE solution, and the final volume of the mixture was diluted to 10 mL.

The recommended extraction procedure was optimized and modeled by CCD and RSM (Mark & Workman, 2007; Stoyanov & Walmsley, 2006). Optimized parameters were the ratio of MSE solution volume to oil mass ($X_1 = R$), mixing time ($X_2 = t$) and temperature ($X_3 = T$). The real values of factors were in the range of 0.16–1.84 mL g^{-1} for ratio of MSE to oil, 3.14–36.82 min. for mixing time, and 13.2–46.8 °C for temperature. Within the scope of optimization, 20 experiments were carried out using solutions containing 20 μg g^{-1} Ni(II) in n-hexane. After separation, Ni(II) concentration of the aqueous phase was determined by FAAS.

In order to investigate accuracy and applicability of the method, spiked and unspiked edible oils were analysed according to the optimized procedure.

2.5. Comparative procedure

Oil samples were mineralized by microwave digestion system prior to ICP-OES determination (Yaşar & Güçer, 2003). External standard calibration was used, and calculated values were compared with results obtained for the proposed method.

3. Result and discussion

For practical use of the proposed method, extraction of Ni(II) from oil should be highly efficient. According to kinetic study at 278 nm, complex formation was completed in 20 min. Stoichiometry of the complex was investigated using continuous variation and determined as 1:1. The molar absorptivity (ε) values for MSE, Ni(II) and Ni-MSE at three different wavelengths were also determined. According to the standard multi-component analysis (Perkampus,

1992), a 3 × 3 matrix was constructed based on ε values for each component. The concentration of free MSE, Ni(II) and Ni-MSE were calculated by solving this matrix. The equilibrium concentrations of MSE, Ni(II) and Ni-MSE were used in:

$$K_f = \frac{[\text{Ni} - \text{MSE}]}{[\text{Ni}^{2+}][\text{MSE}]} \quad (1)$$

and the formation constant (K_f) was calculated as 2.7 (± 0.4) × 10^4. To maintain reproducible and repeatable recovery rates, the MSE solution needed to be buffered at a suitable pH. The effect of pH on Ni(II) extraction was investigated in the range 2–10 using buffered MSE solutions. As expected, and shown in Fig. 2, according to the degradation of the MSE in an acidic medium (pHs < 4) and precipitation of nickel hydroxide at alkaline environment, absorbance was lower. The maximum absorbance of the complex was obtained at pH4. Thus, subsequent studies were performed at this pH.

3.1. Optimization of the proposed method

The ratio of MSE to oil ($X_1 = R$), mixing time ($X_2 = t$) and temperature ($X_3 = T$) were optimized by CCD. The 20 experiments applied within the scope of CCD are given in Table 1. The extracts were separated from the model oil solution were mixed with concentrated HNO_3 at ratio of 5:1 prior FAAS determination.

The empirical y equation, including three factor obtained from the CCD experiments, was:

$$y = 0.239256 - 0.00533R + 0.640264t - 0.01272T - 0.2055R^2 + 0.699612t^2 - 0.19508T^2 - 0.06878Rt + 0.045393RT - 0.00863tT \quad (2)$$

In the y equation, linear terms (R, t and T) indicate first order effects, quadratic terms (R^2, t^2 and T^2) indicate second order effects, and $R\,t$, $R\,T$ and $t\,T$ indicate interactions between factors. By equalization of the derivatives of y equation, in terms of R, t and T to zero, Eqs. (3)–(5) were obtained:

$$\frac{\partial_y}{\partial_R} = -0.0533 - 0.41101R - 0.06878t + 0.045393T = 0 \quad (3)$$

$$\frac{\partial_y}{\partial_t} = 0.640264 + 1.399224t - 0.06878R - 0.00863T = 0 \quad (4)$$

$$\frac{\partial_y}{\partial_T} = -0.01272 - 0.39015T + 0.045393R - 0.00863t = 0 \quad (5)$$

Solutions for these equations were achieved using Microsoft® Excel. The real values of the parameters were calculated as 0.97 mL g^{-1} for the ratio of MSE to oil, 15.4 min. for mixing time and 29.7 °C for temperature.

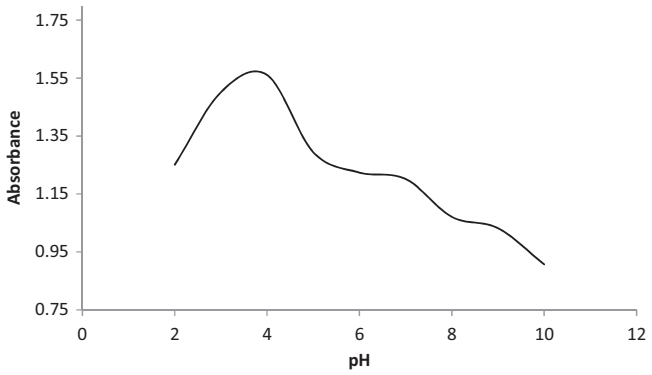

Fig. 2. Effect of pH on complexation.

Table 1
Experimental design and recovery values for Ni(II).

Run	Levels of factors			Added Ni (μg g^{-1})	Found Ni (μg g^{-1})	Recovery (%)	Response (y)
	R (mL g^{-1})	t (min.)	T (°C)				
1	0.50	10.00	20.0	20.00	18.86	94.29	0.1750
2	1.50	10.00	20.0	20.00	20.67	103.35	0.2984
3	0.50	30.00	20.0	20.00	19.46	97.31	0.3713
4	1.50	30.00	20.0	20.00	21.96	109.78	0.1022
5	0.50	10.00	40.0	20.00	17.95	89.76	0.0977
6	1.50	10.00	40.0	20.00	19.30	96.50	0.2853
7	0.50	30.00	40.0	20.00	18.59	92.96	0.1421
8	1.50	30.00	40.0	20.00	21.16	105.82	0.1720
9	1.00	20.00	30.0	20.00	18.39	91.97	0.1245
10	0.16	20.00	30.0	20.00	18.83	94.17	0.1714
11	1.84	20.00	30.0	20.00	17.66	88.28	0.0853
12	1.00	3.14	30.0	20.00	17.10	85.52	0.0690
13	1.00	36.82	30.0	20.00	19.96	99.81	5.3091
14	1.00	20.00	13.2	20.00	18.52	92.61	0.1352
15	1.00	20.00	46.8	20.00	21.11	105.54	0.1805
16	1.00	20.00	30.0	20.00	19.14	95.70	0.2324
17	1.00	20.00	30.0	20.00	18.00	90.00	0.1000
18	1.00	20.00	30.0	20.00	20.54	102.70	0.3698
19	1.00	20.00	30.0	20.00	18.78	93.92	0.1646
20	1.00	20.00	30.0	20.00	19.29	96.47	0.2835

For the graphical interpretation of the interactions, the use of three dimensional (3-D) plots for the regression model is highly recommended (Bas & Boyaci, 2007; Yasini, Shemirani, & Khani, 2012). The 3-D central composite design plots of the response, shown in Fig. 3, were obtained when one of the variables was fixed to central point and the others were allowed to vary. As seen in Fig. 3a, the 3-D plots were enhanced as a function of the ratio of MSE to oil and temperature at constant mixing time. The recovery percentage decreased slightly with reduced temperature due to less formation of the complex. Increasing in the ratio of MSE to oil from 0.5 to 1.5 increased the recovery, as expected. Fig. 3b indicates that extending mixing time increased the yield. Therefore, mixing time is an important factor for extraction of nickel from an oil matrix. The interactions between temperature and mixing time, shown in Fig. 3c, also indicated that mixing time affects the yield.

3.2. Interference studies

The effects of interfering ions on the complexation of nickel in ethanolic aqueous solution were investigated. Model solutions, which include 1×10^{-5} mol L^{-1} Ni(II) and different amounts of Cu^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, K^+, Mn^{2+}, Fe^{3+} across the range 1–100-fold analyte were analysed. Tolerance limits were regarded as interfering ion concentrations causing 5% change in absorbance. The tolerance limits of Zn^{2+}, Mg^{2+}, K^+ and Mn^{2+} ions were 100-fold; Cu^{2+} and Ca^{2+} ions were fivefold complexation of nickel. As expected, only Fe^{3+} ion interfered with complexation of Ni(II) at low interferent-to-analyte (1:1) ratio due to high complexation capacity (Baran & Yaşar, 2010; Tokay & Bağdat, 2015). This interference may be overcome using concentrated MSE.

3.3. Method validation

In order to validate the proposed method, the extraction procedure was implemented with an oil-based Ni(II) standard. Ni(II) content of this solution was analysed using the improved extraction and determination procedures ($n = 10$). The certified value of the solution was 20.0 μg g^{-1} and the value obtained was 18.8 ± 4.3 with 93.8% recovery. The certified results and those obtained experimentally were compared using the Student's t test.

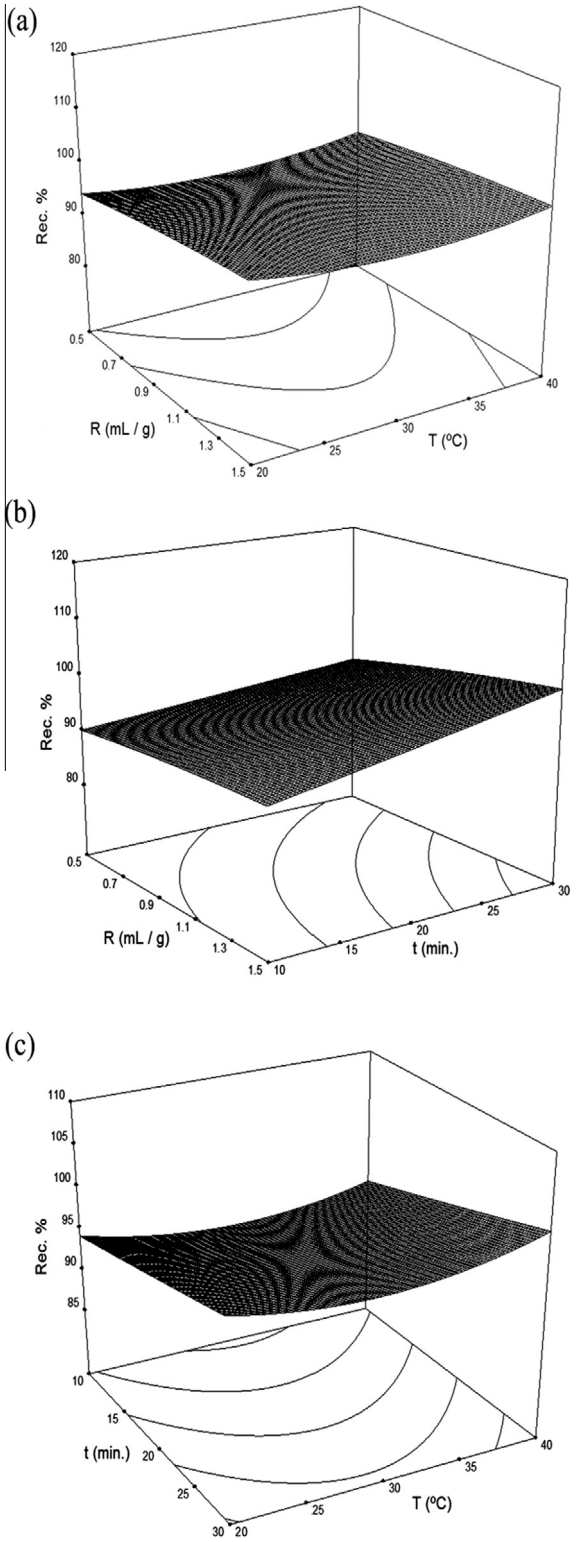

Fig. 3. The 3D CCD plots for the effects of variables on recovery rates: (a) effect of the ratio of Schiff base solution to oil mass and temperature on recovery percentages. Conditions; concentration of Ni(II) 20 μg g^{-1}; mixing time 20 min; ratio of Schiff base solution to oil mass 0.5–1.5 mL g^{-1}; temperature 20–40 °C. (b) Effect of the ratio of Schiff base solution to oil mass and mixing time on recovery percentages. Conditions; concentration of Ni(II) 20 μg g^{-1}; temperature 30 °C; ratio of Schiff base solution to oil mass 0.5–1.5 mL g^{-1}; mixing time 10–30 min. (c) Effect of the temperature and mixing time on recovery percentages. Conditions; concentration of Ni(II) 20 μg g^{-1}; ratio of Schiff base solution to oil mass 1.0 mL g^{-1}; temperature 20–40 °C; mixing time 10–30 min.

Table 2
Results for the determination of Ni(II) in some spiked real samples (n = 3).

Samples	Spiked Ni(II) (μg g^{-1})	Found Ni(II) (μg g^{-1})	Recovery (%)	$\lvert\mu - x\rvert$	$\lvert\frac{ts}{\sqrt{N}}\rvert$
Olive oil	2.00	1.86 ± 0.13	93.02	0.14	0.33
Sunflower oil	2.00	1.84 ± 0.07	92.01	0.16	0.18
Canola oil	2.00	1.93 ± 0.14	96.35	0.07	0.34
Corn oil	2.00	1.91 ± 0.12	95.52	0.09	0.31
Hazelnut oil	2.00	1.94 ± 0.12	96.78	0.06	0.31

Table 3
Raw sample analysis with novel and conventional methods (n = 3).

Samples	Concentration of Ni (μg g^{-1})	
	Suggested method	Conventional method
Olive oil	0.26 ± 0.01	0.31 ± 0.02
Sunflower oil	<LOD	<LOD
Canola oil	<LOD	<LOD
Corn oil	1.06 ± 0.09	0.98 ± 0.03
Hazelnut oil	<LOD	<LOD

t was calculated as 0.75 and t_{critic} is 2.26 at 95% confidence level. The experimental t value was lower than the critical value; so it may be concluded that there was no significant difference between the experimental and theoretical values. The results suggest this easily applicable method has good recovery for Ni(II) determination in an oil matrix. The limit of detection (LOD) and the limit of quantification (LOQ) were defined as the analyte concentration corresponding to absorbance signal equal to three times and ten times the standard deviation of the blank oil. The calculated values were 0.06 and 0.18 μg g^{-1} for LOD and LOQ, respectively.

3.4. Real sample analysis

The improved procedure was implemented with spiked and unspiked plant-derived oil samples. As shown in Table 2, recoveries from the spiked samples were in the range 92.01–96.78%. Recovery was satisfactory, and the difference between theoretical (μ) and experimental ($\bar{x}$) values were less than limit values ($ts/\sqrt{N}$) at 95% confidence level. This means there was no significant difference between theoretical and experimental concentrations.

The unspiked level of Ni(II) was lower than LOD in real samples, except in olive and corn oils. The reported Ni(II) content of edible oils was in the range 10.6 ng g^{-1}–2.26 μg g^{-1} (Bakırcıoğlu, Kurtuluş, & Yurtsever, 2013; Baran & Yaşar, 2012; Yaşar, Baran, & Alkan, 2012). According to this, our results are in agreement with the literature. In addition to the proposed method, a comparative procedure was also applied with real samples and the results are compared in Table 3. Using ICP-OES, Ni(II) content of sunflower, canola and hazelnut oils were below 0.18 μg g^{-1}. Ni(II) content of olive and corn oils was comparable for both methods.

4. Conclusions

Metal analysis in edible oils is very difficult due to the high organic matrix. Therefore, a novel Ni(II) extraction and determination method was developed. The proposed spectrometric method for determination of Ni(II) offers several advantages over previously reported procedures. The results clearly demonstrate that the method is inexpensive, simple and rapid and, since it can be used to determine Ni(II) in oils by FAAS in 20 min, applicable for routine analysis.

Acknowledgements

The authors would like to thank the Scientific and Technological Research Council of Turkey (TUBITAK-TBAG project number 105T153) and Balıkesir University (BAP project number 2009/16) for financial support. Dr. Altan Ercan and Dr. Serdar Sönmez are also gratefully acknowledged for language editing.

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