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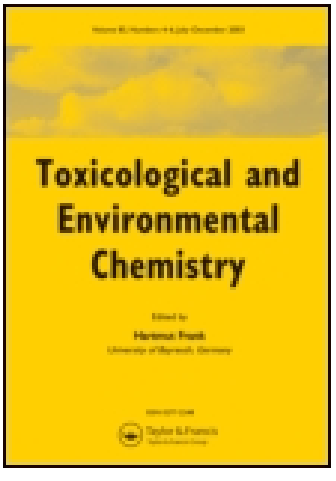

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Cadmium and nickel determinations in some food and water samples by the combination of carrier element-free coprecipitation and flame atomic absorption spectrometry

Zekeriyya Bahadir[a], Duygu Ozdes[b], Volkan Numan Bulut[c], Celal Duran[d], Hamide Elvan[e], Hakan Bektas[a] & Mustafa Soylak[f]

[a] Department of Chemistry, Giresun University, Giresun, Turkey

[b] Gumushane Vocational School, Gumushane University, Gumushane, Turkey

[c] Macka Vocational School, Karadeniz Technical University, Macka, Trabzon, Turkey

[d] Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, Trabzon, Turkey

[e] Reşadiye Vocational School, Gaziosmanpasa University, Reşadiye, Tokat, Turkey

[f] Department of Chemistry, Faculty of Sciences, Erciyes University, Kayseri, Turkey

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Cadmium and nickel determinations in some food and water samples by the combination of carrier element-free coprecipitation and flame atomic absorption spectrometry

Zekeriyya Bahadir[a], Duygu Ozdes[b], Volkan Numan Bulut[c], Celal Duran[d], Hamide Elvan[e], Hakan Bektas[a] and Mustafa Soylak[f]*

[a]*Department of Chemistry, Giresun University, Giresun, Turkey;* [b]*Gumushane Vocational School, Gumushane University, Gumushane, Turkey;* [c]*Macka Vocational School, Karadeniz Technical University, Macka, Trabzon, Turkey;* [d]*Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, Trabzon, Turkey;* [e]*Reşadiye Vocational School, Gaziosmanpasa University, Reşadiye, Tokat, Turkey;* [f]*Department of Chemistry, Faculty of Sciences, Erciyes University, Kayseri, Turkey*

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A procedure for separation and enrichment of Cd(II) and Ni(II) ions based upon carrier element-free coprecipitation by using an organic coprecipitant, 2-{4-[2-(1H-Indol-3-yl)ethyl]-3-(4-methylbenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl}-N′-(3-fluoro-phenylmethyliden) acetohydrazide, prior to their flame atomic absorption spectrometric detections has been developed. The effects of varied experimental conditions on the performance of the developed method such as pH, sample volume, amount of coprecipitating agent, etc. were evaluated in detail on the recovery of analyte ions, and the influences of some anions and cations were investigated. The limits of detection for Cd(II) and Ni(II) ions based on three times the standard deviation of the blanks (*N*: 10) were obtained as 0.70 μg L^{-1} and 1.21 μg L^{-1}, respectively. The accuracy of the method was tested by analyzing a certified reference material and by spike tests. The method was applied to determine the levels of cadmium and nickel in stream and sea water, rice, red lentil, and wheat samples.

Keywords: preconcentration; flame atomic absorption spectrometry; carrier element-free coprecipitation; food; water

1. Introduction

Determination of metals in environmental samples is an important part of analytical chemistry. Nowadays, the pollution by metals is a major interest owing to their potential toxic effects on living organisms (Tuzen et al. 2007, 2009). There has been an increasing interest in studying the toxicity and effect of elements on human health and environment. Cd(II) is one of the most hazardous elements for human health. Cd(II) is known to be excessively toxic even at low concentrations and it can be accumulated in organs such as kidney, liver, and lungs, causing serious problems such as arteriosclerosis and cancer. The World Health Organization (WHO) has set a limit of 3.0 μg L^{-1} for Cd(II) ions in drinking water (WHO 1998; Afridi et al. 2006; Tabrizi 2007). In modern industry, metallic nickel is also widely used. Ni(II) and its compounds of disposal cause environmental pollution. The inhalation and ingestion of Ni(II) and its by-products may cause serious

*Corresponding author. Email: soylak@erciyes.edu.tr

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problems such as lung fibrosis, cardiovascular, and nasopharyngeal diseases (IARC 1990; Kalyakina et al. 2003). Hence, the development of sensitive methods is important for the determination of Cd(II) and Ni(II) ions in water and food samples (Baytak and Turker 2006). Various analytical techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS) (Ataro et al. 2008), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Kagaya et al. 2005), flame atomic absorption spectrometry (FAAS) (Doganlar and Atmaca 2010), and electrothermal atomic absorption spectrometry (ETAAS) (Daftsis and Zachariadis 2007), are widely used for determination of metals in environmental samples. The preferred method for the determination of metal concentrations is FAAS due to its low cost and comparatively simple usage (Srogi 2008). The low concentrations of analyte ions and the interference effects of the matrix components in real samples are the main problems in the determination of metal ions by FAAS. Separation and preconcentration procedures have been efficiently used to solve these problems (Saracoglu, Soylak, and Elci 2001; Uzun et al. 2002; Tian et al. 2010). The commonly used separation and preconcentration methods are cloud point extraction (Xiang et al. 2012), solid-phase extraction (Soylak et al. 2001; Narin et al. 2001), solvent extraction (Lajunen and Kubin 1998), and coprecipitation (Aydin and Soylak 2007). Among them, the coprecipitation method, performed by using various inorganic or organic coprecipitants as efficient collectors of metals, is widely preferred due to its simplicity, lower cost, and high enrichment factors (Saracoglu, Soylak, and Elci 2001). Inorganic coprecipitants such as zirconium (Citak, Tuzen, and Soylak 2009) and iron (Duan et al. 2003) hydroxides and organic ligands like dithiocarbamates (Baysal, Akman, and Calisir 2008) have been used for preconcentration of different metal ions from environmental samples. However, carrier elements (Mg, Ni, Cu) used for the formation of precipitate can interfere during the analytical work. Lately, a new coprecipitation method, carrier element-free coprecipitation (CEFC), has been developed. The CEFC method has many benefits for separation and preconcentration of metals due to the lack of contamination and adsorption risks for metal ions from a carrier element (Bulut et al. 2008; Saracoglu and Soylak 2010). Triazole derivatives are attractive compounds for various analytical chemistry studies as indicator for acid–base titrations (Gundogdu et al. 2008; Bulut et al. 2010) and as coprecipitant for separation and preconcentration of metal ions (Bulut et al. 2008; Duran et al. 2009).

In this paper, the CEFC method was applied for separation and preconcentration of Cd(II) and Ni(II) ions from aqueous media using 2-{4-[2-(1H-Indol-3-yl)ethyl]-3-(4-methylbenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl}-N′-(3-fluoro-phenylmethyliden) acetohydrazide (IMOTFAH) as an organic coprecipitant. The method was applied to determine the cadmium and nickel levels of some food and water samples.

2. Materials and methods

2.1. Apparatus

The determination of Cd(II) and Ni(II) ions was carried out using an atomic absorption spectrometer (AAnalyst 400, Perkin Elmer, Norwalk, CT, USA)with an air-acetylene and a 10-cm-long burner head. The instrumental parameters were set as advised by the manufacturer. The pH of the aqueous solutions was adjusted by using a glass electrode (Hanna pH-211, HANNA instruments, Cluj, Romania). The pH meter was calibrated by using pH 4.0, 7.0, and 10.0 buffer solutions. A centrifuge (3-16P model, Sigma

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Laborzentrifugen, Osterode am Harz, Germany) was used for centrifugation of solutions. A temperature- and pressure-controlled closed-vessel microwave system (Ethos D, Milestore Inc., Bergamo, Italy) at maximum pressure 100 atm, and a maximum temperature of 300 °C was used to digest the solid samples.

2.2. Reagents

All of the chemical reagents used were analytical grade and obtained from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Double-distilled water was used for each dilution. The standard and working solutions of Cd(II) and Ni(II) ions were prepared by the dilution of 1000 mg L^{-1} stock solutions of the given elements purchased from Sigma-Aldrich (Taufkirchen, Germany). The pH adjustments were carried out both by diluted HNO_3 and NaOH solutions. In this study, IMOTFAH was used as a coprecipitating agent. The detailed information of its synthesis was given in the literature (Bektas et al. 2010). A solution of 0.2% (w/v) IMOTFAH in a dimethyl sulfoxide/ethanol (1:1) mixture was prepared. The CRM-SA-C Sandy Soil C certified reference material (CRM) used in the analytical studying was supplied from High-Purity Standard Inc. (Charleston, SC, USA).

2.3. Model work procedure

To optimize the present CEFC procedure, 1.0 mL of 0.2% (w/v) IMOTFAH solution was added into 50 mL of model solutions including 1.0 μg Cd(II) and 5.0 μg Ni(II) ions. Then, the pH of the solution was adjusted to 7.5 by addition of diluted HNO_3 or NaOH solutions. After 20 min of standing time, the solution was centrifuged at 3000 rpm for 5 min. The supernatant was removed. The remaining precipitate in the plastic tube was dissolved in 1.0 mL of concentrated nitric acid. The solution was diluted to 2.0 mL with distilled water and the content of analyte ions in the final volume was determined by FAAS.

2.4. Analysis of real samples

The present CEFC method was applied to analyses of various environmental liquid and solid real samples. The water samples – sea water (Black Sea, Trabzon/Turkey) and stream water (Sana stream, Trabzon/Turkey) – were acidified to pH 2.0 with diluted HNO_3 after collection. The samples (100 mL) were filtered through Millipore cellulose membrane filter (0.45-μm pore size) and the pH values of the water samples were adjusted to 7.5. The CEFC method was performed on the samples after addition of an appropriate amount of 0.2% (w/v) IMOTFAH. The final volumes of the water samples diluted to 2.0 mL with distilled water and the content of Cd(II) and Ni(II) ions were determined by FAAS.

An aliquot of 0.100 g of CRM-SA-C-Sandy Soil C, 0.750 g of rice, wheat, and red lentil samples were weighed into Teflon vessels, separately. Then, 6 mL of HNO_3 and 2 mL of H_2O_2 for rice, wheat, and red lentil samples, 4.5 mL of HCl, 1.5 mL of HNO_3, 1 mL of HF, and 2 mL of H_2O_2 for the CRM-SA-C Sandy Soil C standard were added into the vessels. The digestion conditions for the microwave system were 5 min at 250 W, 6 min at 400 W, 6 min at 650 W, 6 min at 250 W, at 45 bars pressure and ventilation of 3 min. After microwave digestion, the final volumes of the samples were made

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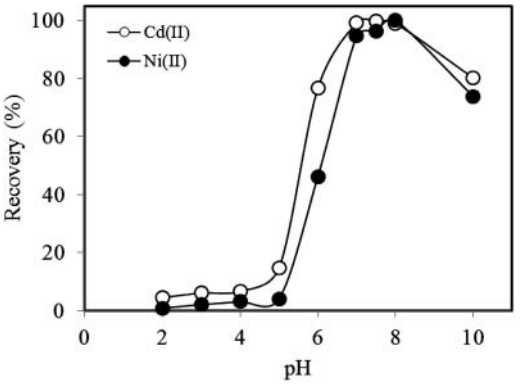

Figure 1. Relationship between the determined levels of analyte recovery and pH (*N*: 3, sample volume: 50 mL, amount of IMOTFAH: 2.0 mg, standing time: 20 min, centrifugation speed: 3000 rpm, centrifugation time: 5 min).

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up to 50 mL with distilled water. The preconcentration procedure described in Section 2.3 was applied to the samples. The levels of the Cd(II) and Ni(II) ions were determined by FAAS after the final volume of the solutions was made up to 2.0 mL with distilled/deionized water.

3. Results and discussion

The effect of pH on the recoveries of Cd(II) and Ni(II) ions was examined in the solution pH range of 2.0–10.0 (Figure 1). Maximum recovery values (>95%) were obtained at pH 7.0–8.0, so all further experiments were performed at pH 7.5.

The effect of the amount of IMOTFAH on the coprecipitation of Cd(II) and Ni(II) ions between 0 mg and 6.0 mg was studied (Figure 2). The recoveries were below 80%

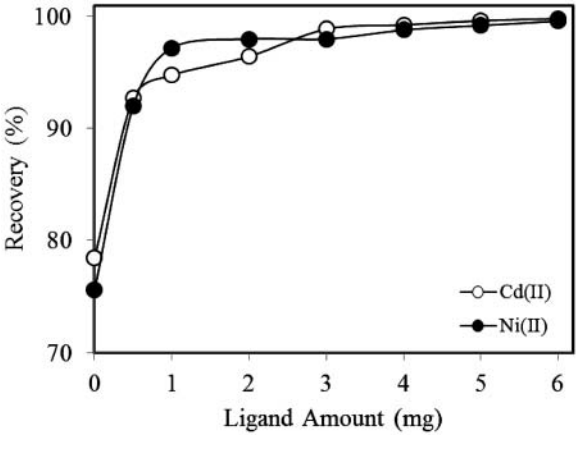

Figure 2. Influences of amount of IMOTFAH on the recovery values of analytes (*N*: 3, pH: 7.5, sample volume: 50 mL).

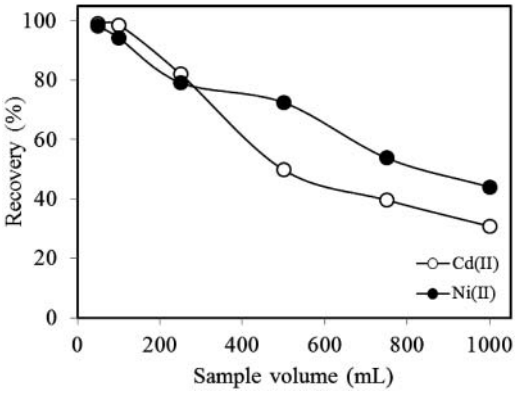

Figure 3. Relationship between sample volume and recoveries of analytes (*N*: 3, pH: 7.5).

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without IMOTFAH but increased with the amount of IMOTFAH. Quantitative recoveries were obtained under the addition of 2.0 mg (1.0 mL of a 0.2% (w/v) solution) of IMOTFAH and this amount was used in all other experiments.

The influence of the sample volume was examined between 50 mL and 1000 mL. For more than 100 mL, the recoveries were not quantitative (Figure 3). Obviously, a preconcentration factor of 50 is achieved when the sample volume is 100 mL and the final volume is 2.0 mL.

The performance of CEFC procedure was also investigated depending upon standing time (0–30 min), centrifugation speed (1000–3500 rpm) and centrifugation time (5–30 min). Quantitative recoveries were obtained for 20 min of standing time and centrifugation at 3000 rpm, for 5 min.

3.1. Effect of matrix ions

"Matrix effects" in the flame atomic absorption spectrometric detection of metal ions is an important problem (Soylak, Akkaya, and Elci 2002; Armagan et al. 2002; Kaplan et al. 2004; Jeong et al. 2010; Zhao et al. 2010). Different amounts of alkali and earth alkali ions and anions were added to the solutions consisting fixed amounts of Cd(II) and Ni(II) ions and the coprecipitation method was applied to these solutions to investigate influences of matrix components. The results are summarized in Table 1. The existence of matrix ions has no notable effect on the separation and preconcentration of Ni(II) and Cd(II) ions under the selected conditions. Eventually, the CEFC method can be performed to the samples that consist of various foreign ions at allowable levels.

3.2. Analytical performance of the method

The precision of the method was evaluated as the relative standard deviation (RSD) obtained after replicated analyzing samples. In order to evaluate the precision of the determination of Cd (II) and Ni(II) ions (1.0 μg Cd(II) and 5.0 μg Ni(II) in 50 mL aqueous solution), the procedure was repeated ten times under optimum conditions mentioned

Table 1. Influences of matrix ions on the recoveries of Cd(II) and Ni(II) (*N*: 3, pH: 7.5, amount of IMOTFAH: 2.0 mg (1.0 mL 0.2% (w/v)), standing time: 20 min, centrifugation rate: 3000 rpm, centrifugation time: 5 min).

			Recovery (%)	
Ions	Added as	Conc.(mg L^{-1})	Cd(II)	Ni(II)
Na^+	NaCl	5000	95.6 ± 3.1	97.3 ± 3.8
K^+	KCl	1000	94.9 ± 1.6	99.6 ± 1.9
Ca^{2+}	$CaCl_2$	500	94.8 ± 1.7	95.6 ± 2.5
Mg^{2+}	$Mg(NO_3)_2$	1000	92.2 ± 1.3	101.6 ± 2.8
NO_3^-	$NaNO_3$	1000	97.4 ± 0.8	101.3 ± 1.9
CO_3^{2-}	Na_2CO_3	500	94.1 ± 1.1	91.3 ± 2.2
SO_4^{2-}	Na_2SO_4	500	94.9 ± 1.9	96.0 ± 3.1
PO_4^{3-}	Na_3PO_4	1000	97.6 ± 2.2	99.3 ± 1.6
Al(III), Fe(III), Pb(II), Zn(II), V(V), Cr(III)	[a]	25	93.8 ± 1.3	101.6 ± 2.2
Mixed[b]			97.1 ± 0.9	98.0 ± 1.6

[a]V(V) is added as V_2O_5; other ions are added as their nitrate salts.
[b]5865 mg L^{-1} Na^+, 9120 mg L^{-1} Cl^-, 1160 mg L^{-1} NO_3^-, 250 mg L^{-1} K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}, and 10 mg L^{-1} Al(III), Fe(III), Pb(II), Zn(II), V(V), and Cr(III).

in Section 2.3. The RSD values for Cd(II) and Ni(II) ions were found to be 2.0 and 3.2, respectively. The limit of detection (LOD) based on three times the standard deviations (*N*: 10) of the blank solutions with the CEFC step was found to be 1.21 μg L^{-1} for Ni(II) and 0.70 μg L^{-1} for Cd(II) ions. The present method is suitable for the determination of Cd(II) and Ni(II) ions in several samples with adequately good recoveries and low RSDs and detection limits.

3.3. Application of the real samples

The validation of the presented method was checked by analyzing a CRM (CRM-SA-C-Sandy Soil C). After 0.1 g of the CRM had been digested with the microwave digestion system, mentioned in Section 2.4, the developed method was applied. The experimental data (101 ± 6 μg g^{-1} for Cd(II), 47.2 ± 2.6 μg g^{-1} for Ni(II)) were in good agreement with the certified values of the CRM (109 ± 8 μg g^{-1} for Cd(II), 48.4 ± 3.0 μg g^{-1} for Ni(II)) and the recovery values were found to be higher than 92%.

The accuracy of the CEFC procedure for the determination of Cd(II) and Ni(II) ion content in different natural waters and solid samples was also tested by applying spike tests. For this aim, different amounts of analyte ions were added in 25 mL of stream and sea water and 0.750 g of rice, red lentil, and wheat samples (Table 2). After application of the present procedure to these samples, the Cd(II) and Ni(II) ion concentrations were determined by direct calibration method. This method could be applied for the separation and preconcentration of Cd(II) and Ni(II) ions in environmental water and solid samples.

The CEFC method was finally applied to the real solid (rice, red lentil, and wheat samples) and liquid samples (sea water and stream water). The results obtained from the real samples are summarized in Table 3.

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Table 2. Test of addition/recovery for Cd(II) and Ni(II) ions from some food and water samples (*N*: 3, pH: 7.5, quantity of IMOTFAH: 2.0 mg, liquid sample volumes: 25 mL, solid sample quantities: 0.75 g, final volumes: 2.0 mL).

		Sea water		Stream water		Rice		Red lentil		Wheat	
Element	Added (μg)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Cd(II)	–	BDL[a]	–	BDL	–	0.31 ± 0.02	–	0.23 ± 0.03	–	0.38 ± 0.04	–
	2.0	1.96 ± 0.05	98.0	1.89 ± 0.10	94.5	2.28 ± 0.03	98.5	2.08 ± 0.25	94.0	2.33 ± 0.03	97.5
	4.0	3.85 ± 0.09	96.2	3.80 ± 0.15	96.0	4.18 ± 0.04	96.7	4.05 ± 0.42	96.2	4.23 ± 0.07	96.2
Ni(II)	–	BDL	–	BDL	–	3.40 ± 0.05	–	1.53 ± 0.05	–	2.20 ± 0.28	–
	5.0	4.93 ± 0.12	98.6	4.53 ± 0.06	90.6	7.90 ± 0.21	90.0	6.45 ± 0.14	98.4	6.90 ± 0.21	94.0
	10.0	9.43 ± 0.60	94.3	9.32 ± 0.32	93.2	12.88 ± 0.25	94.8	10.9 ± 0.21	93.7	11.73 ± 0.32	95.3

[a] Below detection limit.

Table 3. Analyte levels in real samples after being applied the presented procedure (*N*: 3, sample volume: 100 mL, sample quantities: 0.75 g of rice, red lentil, and wheat samples, final volumes: 2.0 mL).

Element	Liquid samples (μg L^{-1})		Solid samples (μg g^{-1})		
	Sea water	Stream water	Rice	Red lentil	Wheat
Cd(II)	4.48 ± 0.11	5.40 ± 0.14	0.41 ± 0.03	0.31 ± 0.04	0.51 ± 0.05
Ni(II)	6.96 ± 0.18	7.45 ± 0.18	4.53 ± 0.07	2.04 ± 0.07	2.93 ± 0.38

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4. Conclusions

The separation and preconcentration method based on CEFC is a simple, economical, and accurate technique for the determination of Cd(II) and Ni(II) ions in rice, red lentil, wheat samples, and stream and sea water samples. We have recommended the use of coprecipitation as an alternative method which combines FAAS with preconcentration of the analyte ions by an organic coprecipitant (IMOTFAH) without carrier element. Therefore, there is no contamination risk from a carrier element. This method is also environment friendly because of the usage of fewer chemicals. The experimental parameters indicated that the presented CEFC method could be successfully applied to routine determination of cadmium and nickel levels in environmental and other food samples with high accuracy and low detection limits.

Acknowledgments

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References

Afridi, H.I., T.G. Kazi, M.K. Jamali, G.H. Kazi, M.B. Arain, N. Jalbani, G.Q. Shar, and A. Sarfaraz. 2006. "Evaluation of Toxic Metals in Biological Samples (Scalp Hair, Blood and Urine) of Steel Mill Workers by Electrothermal Atomic Absorption Spectrometry." *Toxicology and Industrial Health* 22: 381–393.

Armagan, F., M. Soylak, L. Elci, and M. Dogan. 2002. "Solid Phase Extraction of Some Metal Ions on Diaion HP-20 Resin Prior to Flame Atomic Absorption Spectrometric Analysis." *Journal of Trace and Microprobe Techniques* 20:15–27.

Ataro, A., R.I. McCrindle, B.M. Botha, C.M.E. McCrindle, and P.P. Ndibewu. 2008. "Quantification of Trace Elements in Raw Cow's Milk by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)." *Food Chemistry* 111: 243–248.

Aydin, F.A., and M. Soylak. 2007. "A Novel Multi-Element Coprecipitation Technique for Separation and Enrichment of Metal Ions in Environmental Samples." *Talanta* 73: 134–141.

Baysal, A., S. Akman, and F. Calisir. 2008. "A Novel Slurry Sampling Analysis of Lead in Different Water Samples by Electrothermal Atomic Absorption Spectrometry After Coprecipitated with Cobalt/Pyrrolidine Dithiocarbamate Complex." *Journal of Hazardous Materials* 158: 454–459.

Baytak, S., and A.R. Turker. 2006. "Determination of Lead and Nickel in Environmental Samples by Flame Atomic Absorption Spectrometry After Column Solid-Phase Extraction on Ambersorb-572 with EDTA." *Journal of Hazardous Materials* 129: 130–136.

Bektas, H., A. Demirbas, N. Demirbas, and S.A. Karaoglu. 2010. "Synthesis of Some New Biheterocyclic Triazole Derivatives and Evaluation of Their Antimicrobial Activity." *Turkish Journal of Chemistry* 34: 165–180.

Bulut, V.N., C. Duran, A. Gundogdu, M. Soylak, N. Yildirim, and L. Elci. 2008. "A New Approach to Separation and Pre-Concentration of Some Trace Metals with Co-Precipitation Method Using a Triazole." *Talanta* 76: 469–474.

Bulut, V.N., C. Duran, A. Gundogdu, M. Soylak, N. Yildirim, and M. Tufekci. 2010. "A Triazole Derivative as a New Acid-Base Indicator." *Bulletin of the Chemical Society of Ethiopia* 24: 457–460.

Citak, D., M. Tuzen, and M. Soylak. 2009. "Simultaneous Coprecipitation of Lead, Cobalt, Copper, Cadmium, Iron and Nickel in Food Samples with Zirconium(IV) Hydroxide Prior to Their Flame Atomic Absorption Spectrometric Determination." *Food and Chemical Toxicology* 47: 2302–2307.

Daftsis, E.J., and G.A. Zachariadis. 2007. "Analytical Performance of ETAAS Method for Cd, Co, Cr and Pb Determination in Blood Fractions Samples." *Talanta* 71: 722–730.

Doganlar, Z.B., and M. Atmaca. 2010. "Influence of Airborne Pollution on Cd, Zn, Pb, Cu, and Al Accumulation and Physiological Parameters of Plant Leaves in Antakya (in Turkey)." *Water, Air, & Soil Pollution* 214: 509–523.

Duan, T., J. Kang, H. Chen, and X. Zeng. 2003. "Determination of Ultra-Trace Concentrations of Elements in High Purity Tellurium by Inductively Coupled Plasma Mass Spectrometry After $Fe(OH)_3$ Coprecipitation." *Spectrochimica Acta Part B: Atomic Spectroscopy* 58: 1679–1685.

Duran, C., V.N. Bulut, D. Ozdes, A. Gundogdu, and M. Soylak. 2009. "A Novel Method for Speciation of Chromium: Coprecipitation Without Carrier Element by Using a Triazole Derivative." *Journal of AOAC International* 92: 257–262.

Gundogdu, A., V.N. Bulut, C. Duran, B. Kemer, O. Bekircan, and M. Soylak. 2008. "A New ph Indicator Based on 2,5-Diaryl-1-Salicylideneamino-1,3,4-Triazole Derivative." *Chinese Journal of Chemistry* 26: 143–145.

IARC (International Agency for Research on Cancer) [Internet]. 1990. "IARC Monographs on the Evaluation of Carcinogenic Risks to Humans." In: *Chromium, Nickel and Welding*, vol. 49. Lyon: World Health Organization (WHO); [cited Sept 14, 2012]. Accessed Sept 14, 2012. http://apps.who.int/bookorders/anglais/detart1.jsp?sesslan=1&codlan=1&codcol=72&codcch=49

Jeong, E.Y., M.B. Ansari, Y.H. Mo, and S.E. Park. 2010. "Removal of Cu(II) from Water by Tetrakis(4-Carboxyphenyl) Porphyrin-Functionalized Mesoporous Silica." *Journal of Hazardous Materials* 185: 1311–1317.

Kagaya, S., Y. Araki, N. Hirai, and K. Hasegawa. 2005. "Coprecipitation with Yttrium Phosphate as a Separation Technique for Iron(III), Lead, and Bismuth from Cobalt, Nickel, and Copper Matrices." *Talanta* 67: 90–97.

Kalyakina, O.P., O.N. Kononova, S.V. Kachin, and A.G. Kholmogorov. 2003. "Sorption Preconcentration and Determination of Nickel in Wastes of Heat Power Industry by Diffuse Reflection Spectroscopy." *Bulletin of Korean Chemical Society* 24: 173–178.

Kaplan, M., S. Cerutti, S. Moyano, R.A. Olsina, L.D. Martinez, and J.A. Gasquez. 2004. "On-Line Preconcentration System by Coprecipitation with Lanthanum Hydroxide Using Packed-Bed Filter for the Determination of Tellurium in Water by ICP-OES with USN." *Instrumentation Science & Technology* 32: 423–431.

Lajunen, L.H.J., and A. Kubin. 1998. "Determination of Trace Amounts of Molybdenum in Plant Tissue by Solvent Extraction-Atomic-Absorption and Direct-Current Plasma Emission Spectrometry." *Talanta* 33: 265–270.

Narin, I., M. Soylak, L. Elci, and M. Dogan. 2001. "Separation and Enrichment of Chromium, Copper, Nickel and Lead in Surface Seawater Samples on a Column Filled with Amberlite XAD-2000." *Analytical Letters* 34: 1935–1947.

Saracoglu, S., and M. Soylak. 2010. "Carrier Element-Free Coprecipitation (CEFC) Method for Separation and Pre-Concentration of Some Metal Ions in Natural Water and Soil Samples." *Food and Chemical Toxicology* 48: 1328–1333.

Saracoglu, S., M. Soylak, and L. Elci. 2001. "Enrichment and Separation of Traces of Cadmium, Chromium, Lead and Manganese Ions in Urine by Using Magnesium Hydroxide Coprecipitation Method." *Trace Elements and Electrolytes* 18: 129–133.

Soylak, M., Y. Akkaya, and L. Elci. 2002. "Flame Atomic Absorption Spectrometric Determination of Cu(II), Co(II), Cd(II), Fe(III) and Mn(II) in Some Ammonium Salts and Industrial Fertilizers After Preconcentration/Separation on Diaion HP-20." *International Journal of Environmental Analytical Chemistry* 82: 197–206.

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Soylak, M., L. Elci, I. Narin, and M. Dogan. 2001. "Separation and Preconcentration of Gold, Silver and Palladium from Some Aluminum and Manganese Salts on an Activated Carbon Column." *Asian Journal of Chemistry* 13: 699–703.

Srogi, K. 2008. "Developments in the Determination of Trace Elements by Atomic Spectroscopic Techniques." *Analytical Letters* 41: 677–724.

Tabrizi, H.B. 2007. "Development of Cloud Point Extraction-Spectrofluorimetric Method for Trace Copper(II) Determination in Water Samples and Parenteral Solutions." *Journal of Hazardous Materials* 139: 260–264.

Tian, Y., P. Yin, R. Qu, C. Wang, H. Zheng, and Z. Yu. 2010. "Removal of Transition Metal Ions from Aqueous Solutions by Adsorption Using a Novel Hybrid Material Silica Gel Chemically Modified by Triethylenetetraminomethylenephosphonic Acid." *Chemical Engineering Journal* 162: 573–579.

Tuzen, M., D. Citak, D. Mendil, and M. Soylak. 2009. "Arsenic Speciation in Natural Water Samples by Coprecipitation-Hydride Generation Atomic Absorption Spectrometry Combination." *Talanta* 78: 52–56.

Tuzen, M., S. Silici, D. Mendil, and M. Soylak. 2007. "Trace Element Levels in Honeys from Different Regions of Turkey." *Food Chemistry* 103: 325–330.

Uzun, A., M. Soylak, L. Elci, and M. Dogan. 2002. "Application of Sorbent Extraction for Preconcentration/Separation of Trace Amounts of Cadmium (II), Silver (I), Gold (III) and Lead (II) from Metallic Zinc Samples and Their Determinations by Atomic Absorption Spectrometry." *Asian Journal of Chemistry* 14: 1277–1281.

WHO (World Health Organization) [Internet]. 1998. Vol. 2 of *Guidelines for Drinking Water Quality, Health Criteria and Other Supporting Information*. 2nd ed. Geneva: World Health Organization; [cited 2012 Sept 10]. Accessed 2012 Sept 10. http://www.who.int/water_sanitation_health/dwq/2edaddvol2a.pdf

Xiang, G., S. Wen, X. Wu, X. Jiang, L. He, and Y. Liu. 2012. "Selective Cloud Point Extraction for the Determination of Cadmium in Food Samples by Flame Atomic Absorption Spectrometry." *Food Chemistry* 132: 532–536.

Zhao, L., Q. Gong, H. Sun, B. Yang, and Y. Zhu. 2010. "Displacement Solid Phase Extraction as Preconcentration Method for the Determination of Trace Copper in Water Samples by Electrothermal Atomic Absorption Spectrometry." *Atomic Spectroscopy* 31: 201–205.

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