Available online at www.sciencedirect.com
SCIENCE DIRECT®
Food Chemistry 94 (2006) 457–463
Food Chemistry
www.elsevier.com/locate/foodchem

Flow injection chemiluminescence determination of femtogram-level cobalt in egg yolk, fish tissue and human serum

Zhenghua Song *, Qiaoli Yue, Changna Wang

Department of Chemistry, Northwest University, Xi'an 710069, China

Received 20 August 2004; received in revised form 18 November 2004; accepted 2 December 2004

Abstract

Femtogram-level cobalt was determined based on its significantly catalyzed effect on luminol-dissolved oxygen chemiluminescence (CL) reaction in the flow system. The increment of CL signal was proportional to the concentration of cobalt, giving linear range from 10 fg ml^{-1} to 50 pg ml^{-1} ($r^2 = 0.9992$) with a detection limit 4 fg ml^{-1} (3σ). At a flow rate of 2.0 ml min^{-1}, a typical analytical procedure for cobalt, including sampling and washing, could be performed in 0.5 min with a relative standard deviation of less than 3.0%. The proposed method has been successfully applied for the determination of cobalt in egg yolk, fish tissue and human serum, agreed well with radioimmunoassay.

Keywords: Cobalt; Chemiluminescence; Egg yolk; Fish tissue; Serum

1. Introduction

Cobalt is a natural earth element present in trace amount in soil, plants and our diets, which is an essential mineral, although the body only needs a small amount. People are commonly exposed to small amounts of cobalt naturally present in the air they breathe, the water they drink, and the food they eat. Very small amounts of cobalt in people's diets are necessary for good health. As an essential biochemical element, cobalt is mainly stored in red blood cells with smaller amounts in kidney, liver pancreas and spleen (da Silva & Williams, 1991). Research indicates that cobalt helps with the repair of the myelin sheath, increases the effectiveness of glucose transport from the blood into body cells, and increases the assimilation of iron and the building of red blood cells. Cobalt is also an important agent of Vitamin B_{12}; it increases the body's ability to absorb it. And cobalt can stimulate many enzymes of the body and normalize the performance of other body cells. Because of its low absorption rate and high excretion rate, cobalt toxicity is not common, but an excess can lead to enlargement of the thyroid gland (ATSDR, 1992).

Many methods have been reported for the determination of cobalt, including inductively coupled plasma-mass spectrometry (Gao, Oshita, Lee, Oshima, & Motomizu, 2002; Jiann & Presley, 2002; Koplik, Mestek, Kominkova, Borkova, & Suchanek, 2004), atom absorption spectrometry (Lopez-Molinero, Cerbrian, & Castillo, 2004; Manzoori & Bavili-Tabrizi, 2003; Turker & Baytak, 2004), inductively coupled plasma-atom emission spectrometry (Devillers et al., 2002; Guo et al., 2004; Zougagh, Rudner, de Torres, & Cano Pavon, 2004), X-ray fluorescence (Klockenkaemper, Becker, Bubert, Jenett, & von Bohlen, 2002; Roldan, Coll, Ferrero, & Juanes, 2004; Solodukhin et al., 2004), neutron activation analysis (Munita, Nascimento, Schreiber, Luna, &

* Corresponding author. Tel.: +86 29 8830 2054; fax: +86 29 8830 3798.
E-mail address: songzhenghua@hotmail.com (Z. Song).

0308-8146/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2004.12.003

Oliveira, 2004; Tsolakidou & Kilikoglou, 2002); UV–Vis spectrometry (Hejazi, Mohammadi, Yamini, & Brereton, 2004; Paleologos, Prodromidis, Giokas, Pappas, & Karayannis, 2002; Reddy, Radhika, Kumar, Priya, & Rajgopal, 2004; Safavi, Abdollahi, & Hormozi Nezhad, 2002; Sarma, Kumar, Kumar, & Reddy, 2003), high performance liquid chromatography (Dash, Chandrasekaran, Thangavel, Dhavile, & Arunachalam, 2004; Hu, Yang, Yang, & Yin, 2002), and adsorptive stripping voltammetry (Jugade & Joshi, 2003).

Flow injection chemiluminescence (FI-CL) analysis is a versatile, sensitive method with a fairly wide range of applications in many fields, such as environmental, clinical and food chemistry (Roda, Pazzagli, & Kricka, 1999; Roda, Guarigli, Michelini, & Mirasoli, 2003). And the CL methods for the determination of cobalt were also reported, including luminol–hydrogen peroxide system (Campins-Falco, Tortajada-Genaro, Meseguer-Lloret, & Bosch-Reig, 2002; Economou, Clark, & Fielden, 2001; Moliner-Martinez, Meseguer-Lloret, Tortajada-Genaro, & Campins-Falco, 2003; Nakano, Teshima, Kurihara, & Kawashima, 2004; Piza et al., 2002; Tortajada-Genaro, Campins-Falco, & Bosch-Reig, 2003), and luminol-1,10-phenanthroline system (Xiao, Palmer, Wesolowski, Lovitz, & King, 2002). The most of these were employed for the determination of cobalt in potable water, river water, and sea water (Campins-Falco et al., 2002; Moliner-Martinez et al., 2003; Nakano et al., 2004; Segura Carretero, Rodriguez Fernandez, Bowie, & Worsfold, 2000; Tortajada-Genaro et al., 2003; Worsfold et al., 2002). However, no CL method was reported for the determination of cobalt in egg yolk, fish tissue and human serum so far. In this work, it was found that cobalt could greatly catalyze the CL reaction between luminol and dissolved oxygen, and the increment of CL was linear over the cobalt concentration ranging from 10 fg ml^{-1} to 50 pg ml^{-1} with a detection limit of 4 fg ml^{-1} (3σ) and relative standard deviation of less than 3.0%. And the proposed method has been successfully applied for the determination of cobalt in egg yolk, fish tissue and human serum.

2. Experimental section

2.1. Reagents

Cobalt was spectrographically standardized substance (Johnson Matthey & Co., Ltd.). Water was purified in a Milli-Q system (Millipore, Bedford, MA, USA). Luminol (Fluka, Biochemika) was obtained from Xi'an Medicine Purchasing and Supply Station, China. All other chemicals used were of analytical-reagent grade.

A stock solution of cobalt (1.0 mg ml^{-1}) was prepared in 100 ml brown calibrated flask. Luminol supplied as above was used to prepare a 0.25 mol l^{-1} stock standard solution in 0.5 mol l^{-1} sodium hydroxide in a 1000 ml calibrated flask. The standard solutions for calibration were prepared freshly from the stock solution before analysis.

2.2. Apparatus and procedures

A schematic diagram of the flow injection system employed for this work is shown in Fig. 1. The flow manifold included a peristaltic pump (Shanghai meter electromotor plant, Model ND-15, 15 r min^{-1}), which pumped each of all flow streams (including carrier, luminol, NaOH and sample solutions) at a flow rate of 2.0 ml min^{-1}. PTFE tubing (1.0 mm i.d.) was used to connect all components in the flow system. A portion of cobalt was injected quantitatively into carrier stream by a 100 μl loop of six-way valve, until a stable baseline was recorded (at the negative voltage of −725 V). A short mixing tube (10.0 mm in length) was employed for mixing of the cobalt, luminol and NaOH solutions before approaching the flow CL cell. The CL flow cell is a flat spiral consisting glass tubing (2.0 mm i.d., 15.0 cm length) with a volume of 400 μl. The CL signal produced in CL emission cell was detected by photomultiplier tubes (PMT) and a luminosity meter (Xi'an Keri Electron Device Ltd., Model GD-1) without wavelength discrimination, and recorded by a recorder (Shanghai Dahua Instrument and Meter Plant, Model XWT-

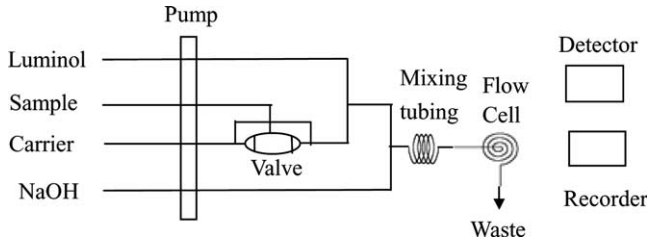

Fig. 1. Schematic diagram of the flow-injection system for determination of cobalt luminol: 1.0×10^{-5} mol l^{-1}; sodium hydroxide: 0.03 mol l^{-1} flow rate: 2.0 ml min^{-1}; high voltage: −725 V.

206). And then the concentration of cobalt was quantified by measuring the increased CL intensity, $\Delta I = I_s - I_o$, where I_o and I_s are CL signals in the absence and in the presence of cobalt, respectively.

2.3. Determination of cobalt in egg yolk and fish tissue

The eggs were purchased from the local market and the dried fish tissue was supplied by Fisheries Research Institute of Shannxi. The samples were pretreated as described in the literature (Lepper, 1950). Approximate 5.0 g of boiled egg yolk was weighed, ground and acidified with 50 ml hydrochloric acid (0.5 mol l^{-1}) in digester. Every sample was digested ultrasonically until homogeneous mixture was obtained; the supernatant solution of centrifuged sample was filtrated at the rate of 4×10^3 r min^{-1}. Also, the dried muscle (1.0 g) and liver (0.2 g) tissue of fish were ground to powder, then mixed with 10 ml hydrochloric acid of 0.5 mol l^{-1}. After ultrasonic homogenization and centrifugation the digested supernatant solution was filtrated. And the resulting sample solutions were determined by the proposed method directly after dilution, respectively.

2.4. Determination of cobalt in human serum

Human serum samples were supplied by Radio-Immunity Center, People's Hospital of Shannxi Province. The following analytical procedure was carried out for dealing with serum samples, 0.1 ml of 0.1 mol l^{-1} hydrochloric acid was added for acidifying 0.1 ml of each sample, and then diluted into 10 ml. And after appropriate dilution, the samples were determined directly by the present method.

3. Results and discussion

3.1. Time profile of CL reaction

Before carrying out in the flow system the time profile of the CL reactions in presence of cobalt (3.0 pg ml^{-1}) and in absence of cobalt were tested with a static CL system. As Fig. 2 (I, II) shows, the cobalt significantly catalyzed the CL reaction between luminol and dissolved oxygen. In the presence of cobalt (curve II) a scintillescent CL signal was observed with obvious increase compared to that in absence of cobalt (curve I).

The CL intensities generated separately by online ultrasonically degassed solutions and general solutions were also tested, and the results indicated the increment of CL intensity was decreased by 97.1% using the degassed solutions, which showed that without dissolved oxygen the reaction could not carry out.

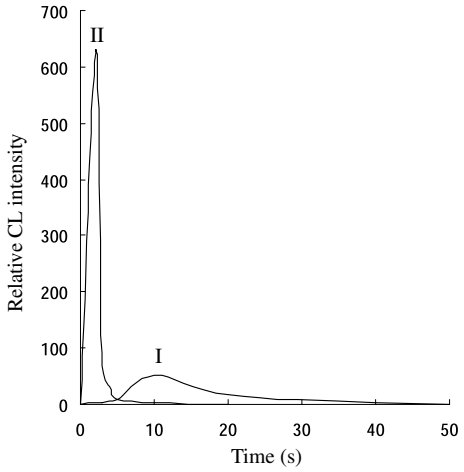

Fig. 2. Kinetic CL-time profile in static system. (I) CL intensity in absence of cobalt. (II) CL intensity in presence of 3.0 pg ml^{-1} cobalt.

3.2. Effect of luminol concentration

The effect of luminol concentration on CL was tested by different concentration of luminol solutions with a series of standard solutions of cobalt from 0.1 to 10.0 pg ml^{-1}. The relationship between increased CL intensity (ΔI) and different concentrations of luminol under the same concentration of cobalt were shown by the regression equations below

$$\Delta I = 18.11 C_{\text{Cobalt}} + 0.3532$$
$$(r^2 = 0.9907, 1.0 \times 10^{-4} \text{ mol } l^{-1} \text{ luminol}),$$

$$\Delta I = 35.08 C_{\text{Cobalt}} - 2.2647$$
$$(r^2 = 0.9945, 1.0 \times 10^{-5} \text{ mol } l^{-1} \text{ luminol}),$$

$$\Delta I = 9.64 C_{\text{Cobalt}} + 6.9428$$
$$(r^2 = 0.9634, 1.0 \times 10^{-6} \text{ mol } l^{-1} \text{ luminol}),$$

$$\Delta I = 1.14 C_{\text{Cobalt}} + 5.8168$$
$$(r^2 = 0.9772, 1.0 \times 10^{-7} \text{ mol } l^{-1} \text{ luminol}).$$

and 1.0×10^{-5} mol l^{-1} luminol possessing the highest sensitivity then was chosen for following experiments.

3.3. Effect of sodium hydroxide concentration

The effect of sodium hydroxide concentration on CL intensity was tested from 5 to 100 mmol l^{-1}, for it is well known that luminol reacts with dissolved oxygen readily in alkaline medium. The experiment was carried out on cobalt of 0.5 pg ml^{-1} to examine the alteration of ΔI. The experimental results showed that ΔI climbed up with the increasing concentration of sodium hydroxide from 5 to 30 mmol l^{-1}, and then decreased with the concentration from 30 to 100 mmol l^{-1}. The decrease of ΔI

under high sodium hydroxide concentration might owe to the formation of unsolvable compounds of cobalt, which leads to decrease of cobalt concentration and rather high background. Thus, 30 mmol l^{-1} sodium hydroxide was selected as an optimum condition for determination of cobalt considering the reagents consumption and determination sensitivity.

3.4. Effect of sample pH on CL

The effect of sample pH on CL was tested by determining sample (containing 2.0 pg ml^{-1} cobalt) under pH from 1.2 to 6.0. The CL intensity increased dramatically with the sample pH lower than 2.9, while the CL intensity did not vary significantly with pH from 2.9 to 6.0. And the samples pH was adjusted into the range of pH 2.9–6.0 for the following experiments.

3.5. Effect of the length of mixing tubing and flow rate

The effect of mixing tube on CL intensity was tested from 0.5 to 6 cm. And the CL intensity was found to be stronger using 1.0 cm of mixing tube than that using any other length of mixing tube. Thus, the length of 1.0 cm mixing tube was then selected regarding sensitivity. The effect of flow rate on determination was tested by investigating the signal-to-noise ratio under different flow rate. And the flow rate of 2.0 ml min^{-1} offering highest signal-to-noise ratio was then chosen as suitable condition considering precision.

3.6. Performance of proposed method for cobalt measurements

A series of standard solutions of cobalt were injected into the manifold depicted in Fig. 1. The increase of CL intensity was found to be proportional with the concentration of cobalt, offering the linearity from 10 fg ml^{-1} to 50 pg ml^{-1} with the detection limit of 4.0 fg ml^{-1} (3σ). And the regression equation is

$$\Delta I = 33.94C_{\text{Cobalt}} + 3.42, r^2 = 0.9992.$$

The relative standard deviations of five determinations were 2.85%, 2.24%, 2.03% and 1.56% with cobalt concentration of 0.03, 0.3, 3.0 and 30.0 pg ml^{-1}, respectively. At a flow rate of 2.0 ml min^{-1}, the determination of analyte could be performed in 0.5 min, including sampling and washing, giving a throughput of 120 h^{-1}.

3.7. Interference studies

The interference of foreign substances were tested by analyzing a standard solution of cobalt (0.2 pg ml^{-1}) to which increasing amounts of interfering analyte was added. The tolerable concentration with respect to 0.2 pg ml^{-1} cobalt for interference at 5% level were less than 5.0 μg ml^{-1} for Cl^-, NO_3^-, Ac^-, I^-, SO_4^{2-}, PO_4^{3-}, BrO_3^-, amylum, glucose, borate, oxalate, malic acid, and 2.5 μg $ml^{-1}$for NH_4^+, Mg^{2+}, Ca^{2+}, methanol, ethanol, glutin, Tween-80, CTMAB, and 0.5 μg ml^{-1} for Ba^{2+},

Table 1
Determination of cobalt in egg yolk[a]

Egg yolk	Added (pg ml^{-1})	Found (pg ml^{-1})	RSD (%)	Recovery (%)	t test ($t_{0.05,4} = 2.78$)	Content of cobalt (μg/kg)
1	0	0.43	2.36	97.2	1.35	4.34
	0.1	0.56	2.15			
2	0	0.41	2.36	98.6	1.74	4.13
	0.1	0.51	1.32			
3	0	0.43	2.36	98.7	1.14	4.29
	0.1	0.53	0.81			
4	0	0.43	2.36	104.7	1.51	4.33
	0.2	0.61	1.91			
5	0	0.43	2.58	109.5	1.69	4.34
	0.2	0.65	1.87			
6	0	0.43	2.36	104.0	0.73	4.32
	0.2	0.64	1.14			
7	0	0.44	2.67	102.5	0.76	4.37
	0.3	0.70	1.67			
8	0	0.43	2.36	96.2	0.60	4.33
	0.3	0.72	1.93			
9	0	0.43	2.24	96.7	1.15	4.29
	0.3	0.66	1.49			

[a] The average of five determinations.

Table 2
Determination of cobalt in fish tissue[a] (liver and muscle)

Fish tissue	Added (pg ml^{-1})	Found (pg ml^{-1})	RSD (%)	Recovery (%)	t test ($t_{0.05,4}$ = 2.78)	Content of cobalt (μg/kg)
Liver 1	0	0.41	2.98	107.6	2.00	4.08
	0.1	0.51	1.25			
Liver 2	0	0.41	2.98	100.3	0.82	4.14
	0.2	0.61	1.48			
Liver 3	0	0.41	2.46	97.3	0.81	4.13
	0.3	0.71	2.04			
Muscle 1	0	0.12	2.73	101.9	4.18	0.23
	0.1	0.22	2.06			
Muscle 2	0	0.11	2.58	96.5	1.15	0.22
	0.2	0.30	1.87			
Muscle 3	0	0.11	2.32	99.9	0.62	0.22
	0.3	0.41	1.56			

[a] The average of five determinations.

Table 3
Results for the determination of cobalt in human serum[a]

Serum no.	Added (fg ml^{-1})	Found (fg ml^{-1})	RSD (%)	Recovery (%)	Content of cobalt (pg ml^{-1})	
					By proposed method	By RIA[b]
1	0	16	2.36	93.3	15.91	15.96
	13	28	2.15			
2	0	15	2.82	103.9	15.22	15.13
	22	38	1.33			
3	0	12	2.88	107.8	12.35	12.65
	44	59	1.46			
4	0	18	2.65	95.6	18.39	18.04
	17	35	1.16			
5	0	17	2.08	105.9	16.96	16.57
	22	40	1.83			
6	0	17	2.26	102.5	16.91	16.78
	44	62	1.18			
7	0	17	2. 62	94.3	17.52	17.61
	17	36	1.64			
8	0	17	2.11	102.1	16.91	16.61
	22	40	1.63			
9	0	14	2.77	106.4	13.66	13.92
	44	60	1.12			

[a] The average of five determinations.
[b] The results were supplied by Radio-Immunity Center, People's Hospital Shannxi Province.

Pb^{2+}, urea, tartrate, 0.1 μg ml^{-1} for Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, Fe^{2+}/Fe^{3+}, respectively.

4. Applications

4.1. Determination of cobalt in egg yolk and fish tissue

Cobalt existing in egg yolk, fish muscle and liver, was determined by the proposed CL method. The results were summarized in Tables 1 and 2. From the tables, cobalt in egg yolk is 4.33 ± 0.04 μg/kg, while contained in fish liver is 4.11 ± 0.03 μg/kg, which is about twenty times of that in fish muscle (0.22 ± 0.01 μg/kg), and the recovery was tested varying from 96.2% to 109.5%. The content of cobalt in egg yolk and fish liver is equivalent to the reference (Ziegler & Filer, 1996) content at 1.31–4.35 μg/kg.

4.2. Determination of cobalt in human serum

According to Section 2, the human serum samples were determined by the proposed method with standard addition. And the samples were also analyzed by

radioimmunoassay (RIA) with a gamma counter (Cap RIA-16, Capintec Instruments, Inc.) in the Radioimmunity counter. The results obtained from the two methods were listed in Table 3 with good agreement, and the relationship equation between them was: $C_{CL} = 1.10C_{RIA} - 1.60$, $r^2 = 0.9925$.

5. Conclusions

A fast and sensitive flow injection CL method has been presented for determining cobalt at femtogram level in egg yolk, fish tissue and human serum samples with successful results.

Acknowledgments

The authors gratefully acknowledge financial support from Shannxi Province Nature Science Foundation and Ministry of Education, China, Grant Nos. 2003B15 and 04Jk103.

References

ATSDR. (1992). Toxicological Profile for Cobalt. Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, Public Health Services, Atlanta, GA.

Campins-Falco, P., Tortajada-Genaro, L. A., Meseguer-Lloret, S., & Bosch-Reig, F. (2002). Multivariate calibration applied to simultaneous chemiluminescence. *Analytical and Bioanalytical Chemistry, 374*(7–8), 1223–1229.

da Silva, J. J. R. F., & Williams, R. J. P. (1991). *The biological chemistry of the elements*. Oxford: Clarendon Press.

Dash, K., Chandrasekaran, K., Thangavel, S., Dhavile, S. M., & Arunachalam, J. (2004). Determination of trace metallic impurities in high-purity quartz by ion chromatography. *Journal of Chromatography A, 1022*(1), 25–31.

Devillers, J., Dore, J. C., Marenco, M., Poirier-Duchene, F., Galand, N., & Viel, C. (2002). Chemometrical analysis of 18 metallic and non-metallic elements found in honeys sold in France. *Journal of Agricultural and Food Chemistry, 50*(21), 5998–6007.

Economou, A., Clark, A. K., & Fielden, P. R. (2001). Determination of cobalt by chemiluminescence after in situ electrochemical preseparation on a flow-through mercury film electrode. *Analyst, 126*(1), 109–113.

Gao, Y. H., Oshita, K., Lee, K. H., Oshima, M., & Motomizu, S. (2002). Development of column-pretreatment chelating resins for matrix elimination/multi-element determination by inductively coupled plasma-mass spectrometry. *Analyst (Cambridge, UK), 127*(12), 1713–1719.

Guo, Y., Din, B. J., Liu, Y. W., Chang, X. J., Meng, S. M., & Liu, J. H. (2004). Preconcentration and determination of trace elements with 2-aminoacetylthiophenol functionalized Amberlite XAD-2 by inductively coupled plasma-atomic emission spectrometry. *Talanta, 62*(1), 209–215.

Hejazi, L., Mohammadi, D. E., Yamini, Y., & Brereton, R. G. (2004). Solid-phase extraction and simultaneous spectrophotometric determination of trace amounts of cobalt, nickel and copper using partial least squares regression. *Talanta, 62*(1), 185–191.

Hu, Q. F., Yang, G. Y., Yang, J. H., & Yin, J. Y. (2002). Study on determination of iron, cobalt, nickel, copper, zinc and manganese in drinking water by solid-phase extraction and reversed-phase HPLC with 2-(2-quinolinylazo)-5-diethylaminophenol as pre-column derivatizing reagent. *Journal of Environmental Monitoring, 4*(6), 956–959.

Jiann, K. T., & Presley, B. J. (2002). Preservation and determination of trace metal partitioning in river water by a two-column ion exchange method. *Analytical Chemistry, 74*(18), 4716–4724.

Jugade, R., & Joshi, A. P. (2003). Trace determination of nickel and cobalt by adsorptive stripping voltammetry using 1-nitroso-2-naphthol. *Indian Journal of Chemistry, Section A: Inorganic, Bio-Inorganic, Theoretical & Analytical Chemistry, 42A*(1), 94–96.

Klockenkaemper, R., Becker, H. W., Bubert, H., Jenett, H., & von Bohlen, A. (2002). Depth profiles of a shallow implanted layer in a silicon wafer determined by different methods of thin-layer analysis. *Spectrochimica Acta, Part B, 57*(10), 1593–1599.

Koplik, R., Mestek, O., Kominkova, J., Borkova, M., & Suchanek, M. (2004). Effect of cooking on phosphorus and trace elements species in peas. *Food Chemistry, 85*(1), 31–39.

Lepper, H. A., (1950). Methods of Analysis of The Association of Official Agriculture Chemists (7th ed.).

Lopez-Molinero, A., Cerbrian, M. A., & Castillo, J. R. (2004). Flame AAS determination of metals in complex paint driers using microwave sample mineralization. *Atomic Spectroscopy, 25*(1), 44–51.

Manzoori, J. L., & Bavili-Tabrizi, A. (2003). Cloud point preconcentration and flame atomic absorption spectrometric determination of cobalt and nickel in water samples. *Microchimica Acta, 141*(3–4), 201–207.

Moliner-Martinez, Y., Meseguer-Lloret, S., Tortajada-Genaro, L. A., & Campins-Falco, P. (2003). Influence of water sample storage protocols in chemiluminescence detection of trace elements. *Talanta, 60*(2–3), 257–268.

Munita, C. S., Nascimento, A., Schreiber, S. B., Luna, S., & Oliveira, P. M. S. (2004). Chemical study of some ceramics from Brazilian Northeast. *Journal of Radioanalytical and Nuclear Chemistry, 259*(2), 305–309.

Nakano, S., Teshima, N., Kurihara, M., & Kawashima, T. (2004). Flow-injection determination of trace elements by using catalysed reactions. *Japanese Bunseki Kagaku, 53*(4), 255–269.

Paleologos, E. K., Prodromidis, M. I., Giokas, D. L., Pappas, A. C., & Karayannis, M. I. (2002). Highly selective spectrophotometric determination of trace cobalt and development of a reagentless fiber-optic sensor. *Analytica Chimica Acta, 467*(1–2), 205–215.

Piza, N., Miro, M., de Armas, G., Becerra, E., Estela, J. M., & Cerda, V. (2002). Implementation of chemiluminescence detection in the multisyringe flow injection technique. *Analytica Chimica Acta, 467*(1–2), 155–166.

Reddy, B. R., Radhika, P., Kumar, J. R., Priya, D. N., & Rajgopal, K. (2004). Extractive spectrophotometric determination of cobalt in synthetic and pharmaceutical samples using Cyanex 923. *Analytical Sciences, 20*(2), 345–349.

Roda, A., Pazzagli, M., & Kricka, LJ. (1999). *Bioluminescence and chemiluminescence perspectives for the 21st century*. Chichester, UK: Wiley.

Roda, M., Guarigli, E., Michelini, M., & Mirasoli, P. (2003). Pasini, analytical bioluminescence and chemiluminescence. *Analytical Chemistry, 75*, 463A–470A.

Roldan, C., Coll, J., Ferrero, J. L., & Juanes, D. (2004). Identification of overglaze and underglaze cobalt decoration of ceramics from Valencia (Spain) by portable EDXRF spectrometry. *X-Ray Spectrometry, 33*(1), 28–32.

Safavi, A., Abdollahi, H., & Hormozi Nezhad, M. R. (2002). Indirect kinetic spectrophotometric determination of cobalt based on the

redox reaction with iron (III) in the presence of 1,10-phenanthroline. *Spectroscopy Letters, 35*(5), 681–688.

Sarma, L. S., Kumar, J. R., Kumar, C. J., & Reddy, A. V. (2003). A sensitive extractive spectrophotometric determination of cobalt in real samples using pyridoxal-4-phenyl-3-thiosemicarbazone. *Analytical Letters, 36*(3), 605–618.

Segura Carretero, A., Rodriguez Fernandez, J., Bowie, A. R., & Worsfold, P. J. (2000). Acquisition of chemiluminescence spectral profiles using a continuous flow manifold with two dimensional CCD detection. *Analyst* (Cambridge, U.K.)*, 125*(3), 387–390.

Solodukhin, V. P., Poznyak, V. L., Kazachevskiy, I. V., Kynazev, B. B., Lukashenko, S. N., & Khazhekber, S. (2004). Some peculiarities of the contamination with radionuclides and toxic elements of the Syrdarya river basin, Kazakhstan. *Journal of Radioanalytical and Nuclear Chemistry, 259*(2), 245–250.

Tortajada-Genaro, L. A., Campins-Falco, P., & Bosch-Reig, F. (2003). Analyser of chromium and/or cobalt. *Analytica Chimica Acta, 488*(2), 243–254.

Tsolakidou, A., & Kilikoglou, V. (2002). Comparative analysis of ancient ceramics by neutron activation analysis, inductively coupled plasma-optical-emission spectrometry, inductively coupled plasma-mass spectrometry, and X-ray fluorescence. *Analytical and Bioanalytical Chemistry, 374*(3), 566–572.

Turker, A. R., & Baytak, S. (2004). Use of *Escherichia coli* immobilized on amberlite XAD-4 as a solid-phase extractor for metal preconcentration and determination by atomic absorption spectrometry. *Analytical Sciences, 20*(2), 329–334.

Worsfold, P. J. et al. (2002). Integrated luminometer for the determination of trace metals in seawater using fluorescence, phosphorescence and chemiluminescence. *Journal of Automated Methods and Management in Chemistry, 24*(2), 41–47.

Xiao, C. B., Palmer, D. A., Wesolowski, D. J., Lovitz, S. B., & King, D. W. (2002). Carbon dioxide effects on luminol and 1,10-phenanthroline chemiluminescence. *Analytical Chemistry, 74*(9), 2210–2216.

Ziegler, E. E., & Filer, L. J. (1996). *Present knowledge in nutrition* (7th ed.). Washington, DC: ILSI Press, pp. 185–199.

Zougagh, M., Rudner, P. C., de Torres, A. G., & Cano Pavon, J. M. (2004). On-line preconcentration and determination of cobalt by DPTH-gel chelating microcolumn and flow injection inductively coupled plasma atomic emission spectrometry. *Analytical and Bioanalytical Chemistry, 378*(2), 423–428.