

The Spectrophotometric and Derivative Spectrophotometric Determination of Cobalt in the Presence of Large Amounts of Nickel Using Br-PADAP

Sérgio L. C. Ferreira^a and Djane S. de Jesus^b

^a Instituto de Química, Universidade Federal da Bahia, 40170-290, Brazil

^b Centro Federal de Educação Tecnológica da Bahia, 40300-010, Brazil

Received: April 20, 1995; October 30, 1995

O presente trabalho descreve o uso de 2-(5-bromo-2-piridylazo)-5-diethylaminophenol (Br-PADAP) na determinação espectrofotométrica de cobalto na presença de grandes quantidades de níquel. O Br-PADAP reage com o íon cobalto(II), formando um complexo vermelho com máximo de absorção em 589 e 567 nm. Foram estudados os seguintes parâmetros: estabilidade do complexo, efeito do pH, quantidade de Br-PADAP, quantidade de tampão acetato, efeito de EDTA, ordem de adição dos reagentes e obediência à lei de Beer. Os resultados demonstraram que cobalto pode ser determinado na presença de grandes quantidades de níquel, em pH 4.0, com uma absorvidade molar de 8.30×10^4 L/mol/cm (em 589 nm). A lei de Beer é obedecida pelo menos até 0.80 µg/mL. O níquel também reage com o Br-PADAP, mas o complexo formado é completamente decomposto após adição de EDTA. O método proposto foi usado na determinação de cobalto em vários sais de níquel, e os resultados encontrados, comparados por ICP, não exibiram diferenças significativas em exatidão e precisão durante a aplicação de testes estatísticos.

The present work describes the use of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) as the spectrophotometric reagent for cobalt determination in nickel and its matrices. Br-PADAP reacts with cobalt(II) forming a red complex with absorption maxima at 589 and 567 nm. The following parameters were studied: complex stability, pH effect, amount of Br-PADAP, amount of acetate buffer, EDTA effect, order of the addition of reagents, and obedience to Beer's Law. The results demonstrated that Br-PADAP can be used for cobalt determination in the presence of large amounts of nickel, at pH 4.0, with a molar absorptivity of 8.30×10^4 L/mol/cm (at 589 nm). Beer's Law is obeyed for at least 0.80 µg/mL. Br-PADAP also reacts with nickel, but the complex formed completely decomposes after addition of EDTA. The proposed procedure was used for cobalt determination in several nickel matrices. The results obtained for cobalt by the Br-PADAP method and the ICP method were statistically compared by means of the Student t-test and the variance ratio F-test, and no significant difference was found.

Keywords: cobalt determination, spectrophotometry, nickel matrices

Introduction

Cobalt is an element nearly always present at trace levels in nickel and its compounds. However, the spectrophotometric determination of this element in these matrices is problematic because many of the indicated reagents also react with nickel. Numerous methods have been published, but normally these methods are not simple and usually require extensive and laborious steps for the separation of

cobalt from nickel, involving operations such as extraction¹⁻⁸, ionic exchange^{9,10}, chromatography¹¹, precipitation of nickel as hexaaminoperchlorate¹², and as dimethylglyoximate¹³ etc. Thus, many of these methods have low reliability. In the present paper, we propose a procedure using Br-PADAP for cobalt determination in large amounts of nickel, using EDTA as the masking agent. The proposed method is simple, highly selective, reproducible and presents little reagent manipulation. The derivative

procedure allows cobalt determination with a detection limit lower than the conventional procedure. Table 1 describes the application of some reagents during cobalt determination in nickel matrices.

Br-PADAP is a good spectrophotometric reagent for cobalt, and has been indicated for cobalt determination in several papers. Zbíral and Sommer¹⁶ proposed a procedure for cobalt determination in cyanocobalamine and potable waters. The cobalt(III) ion forms a stable complex with Br-PADAP at pH 7, and after a certain time the addition of concentrated hydrochloric, nitric or sulfuric acid to the system, decomposes the Br-PADAP chelates, such as iron(II), iron(III) and zinc(II). In this procedure nickel(II), vanadium(V), copper(II) and palladium(II) seriously interfere. Huo¹⁷ has used Br-PADAP for cobalt determination in iron and steel, forming the cobalt complex in the presence of fluoride ammonium after adding sulfuric acid to mask interferences. Miura¹⁸ studied the application of several masking agents for the spectrophotometric determination of cobalt, iron and manganese with Br-PADAP. A combination of pyrophosphate and ethylene glycol bis(2-aminoethyl ether)-N,N,N',N'-tetraacetic acid (EGTA) was useful for the determination of cobalt(II) in soil and steel samples; EDTA was not investigated as the masking agent,

and nickel(II) ions were not masked by any of the masking agents tested, except for α -picolinic acid, which also reacted with cobalt(II) ions. Ping¹⁹ used Br-PADAP for the simultaneous spectrophotometric determination of trace cobalt and nickel in geological samples; cobalt(II) and nickel(II) ions reacted with Br-PADAP at pH 10, and the complexes formed were extracted using a mixture of benzene-butanol.

Experimental

Reagents

All reagents were of analytical reagent grade unless otherwise stated.

The *Cobalt (II) solution* (1000 $\mu\text{g}\cdot\text{mL}$) was prepared by dissolving pure cobalt (99.99%) in diluted nitric acid with heating and dissolution up to 1 L with demineralized water.

The *Br-PADAP solution* (0.025%) was prepared by dissolving 0.0625 g (Aldrich) in 10 mL of ethanol and 100 mL of Triton-X100 solution (8%) and dissolution up to 250 mL with demineralized water.

The *Buffer solution* (pH 4.0) was prepared by mixing 20.5 g of trihydrate sodium acetate and 49.9 mL of glacial acetic acid in 1 L of demineralized water.

Table 1. Reagents used for cobalt determination in nickel matrices.

Reagent	Separation of nickel from cobalt	Medium	ϵ	References
Diethyldithiocarbamate	extraction	carbon tetrachloride	1.57×10^4	1
1-Nitroso- 2-naphtol	extraction	benzene	3.0×10^4	2
2-Nitroso- 1-naphtol	extraction	toluene	2.6×10^4	3
β -Nitroso- α -naphtol	extraction	chloroform	2.65×10^4	4
PAN	extraction	chloroform	2.5×10^4	5
PAN	extraction	chloroform	2.5×10^4	6
Thiocyanate	extraction	MIBK		7
Thiocyanate	extraction	chloroform		8
Nitritotriacetic acid	anion exchange			9
Nitroso-R salt	anion exchange		2.3×10^4	10
Ethylenediamine	chromatography	-	-	11
Nitroso-R salt*	Ni precipitation		2.3×10^4	12
MPPP**	Ni precipitation	-	3.98×10^4	13
4-(5-Bromo)-2-TAR***	Co coprecipitation			14
Molybdophosphoric acid	none			15
Br-PADAP	none	TRITON-X100	8.30×10^4	this work

ϵ molar absorptivity.

* Ni precipitation as hexamminoperchlorate.

** Ni precipitation as dimethylglyoximate.

*** Co co-precipitation with Al hydroxide.

MPPP 2-(3-methyl-5-propyl-2-pyrrolyl)phenol.

The EDTA solution (0.10 M) was prepared by dissolving 37.22 g of EDTA disodium salt (Merck) and dissolution up to 1 L with demineralized water.

Apparatus

The absorption spectra, first-derivative spectra and absorbances were recorded and measured with a VARIAN DMS-80 spectrophotometer and an INTRALAB recorder using 1.0 cm cells.

The cobalt determination in nickel matrices by atomic emission spectroscopy²² was done using an Applied Research Laboratories 3410 ICP.

A 300 ANALYSER pH meter was used to measure the pH values.

General Procedure

Spectrophotometric determination of cobalt

A portion of solution containing 5.00 μg of cobalt(II) was transferred to a 25 mL standard flask, and 2.5 mL of acetate buffer (pH 4.0) and 5.0 mL of Br-PADAP solution were added. The solution was mixed and after 30 min 2.5 mL of EDTA solution was added. The solution was diluted to the mark with water and the absorbance at 589 nm was measured in a 1.0 cm cell, using an appropriate blank.

First-derivative spectrophotometry

A portion of the solution containing 1.00 μg of cobalt(II) was transferred to a 25 mL standard flask, and 2.5 mL of acetate buffer (pH 4.0), and 5.0 mL Br-PADAP solution was added. The solution was mixed and after 30 min 2.5 mL of EDTA solution was added. The solution was diluted to the mark with water, mixed and the first-derivative spectrum from 800 to 400 nm was recorded against an appropriate blank, at a scan speed of 100 nm/min with slit of 4 nm.

The first-derivative signal amplitude (H) was measured with the recorder voltage at 2 or 5 mv.

Results and Discussion

Characteristics of the reagent and the complex

The reaction of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) with cobalt(II) cation in the presence of Triton-X100 forms a red complex with absorption maxima at 589 and 567 nm, and a composition of 1:2 cobalt(II)-Br-PADAP. The absorbance of the complex reaches a maximum after 30 min of mixing the reagents, and is stable for at least 24 h. The Br-PADAP reagent has an absorption maximum at 487 nm (at pH 4.0). The reagent and its cobalt(II) complex present low solubility in water but the reaction in the presence of Triton-X100 resolves this inconvenience.

Effect of the pH

The effect of pH on the cobalt(II)-Br-PADAP system was studied and the results demonstrated that the absorbance maximum is constant in a pH range of 3.5 to 6.0, as can be seen in Fig. 1. The procedure for cobalt determination in the presence of large amounts of nickel indicates pH 4.0, because at this pH the decomposition of the Ni(II)-Br-PADAP complex with the addition of EDTA is faster. At pH 4.75, the decomposition happens in 180 min, but at pH 4.0 only 90 min is needed. The pH control was done using acetate buffer. The effect of the buffer concentration on the cobalt(II)-Br-PADAP complex was studied, and the results demonstrated that when the buffer is in the concentration range of 0.15-0.60 M in acetate the absorbance signal of the system is not affected (Fig. 2).

Effect of the order of addition of reagents on the complex formation

The order of the addition of the reagents was studied and the results demonstrated that it affects the complex formation (Table 2). The EDTA must be added after the formation of the cobalt(II)-Br-PADAP complex, which is only formed after 30 min of reaction between cobalt(II) ions and Br-PADAP.

Effect of EDTA on the Co(II)-Br-PADAP complex

Br-PADAP is not a selective reagent for cobalt determination. However, the use of EDTA as a masking agent

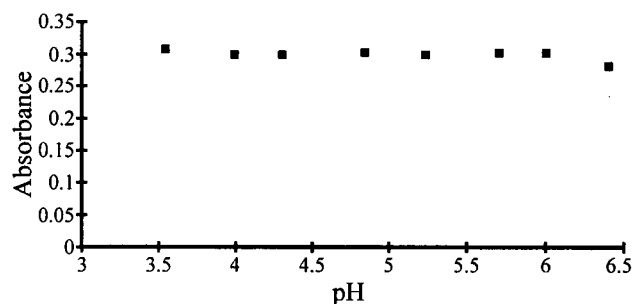


Figure 1. Effect of pH on the Co(II)-Br-PADAP system. $[\text{Co}^{+2}] = 5.0 \mu\text{g}/25.00 \text{ mL}$.

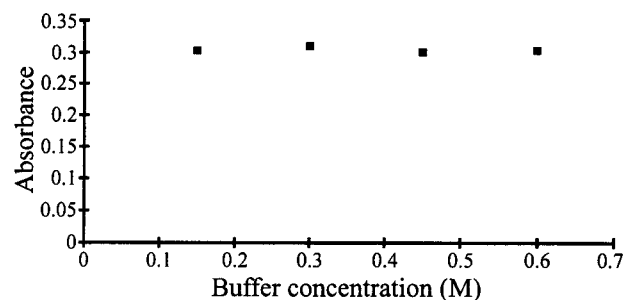


Figure 2. Effect of the buffer amount on the Co(II)-Br-PADAP system. $[\text{Co}^{+2}] = 5.0 \mu\text{g}/25.00 \text{ mL}$.

Table 2. Effect of the order of addition.

Order of addition	Absorbance
Co(II) + BR-PADAP + EDTA + buffer	0.005
Co(II) + BR-PADAP + buffer + EDTA	0.009
Co(II) + EDTA + buffer + BR-PADAP	0.000
Co(II) + EDTA + BR-PADAP + buffer	0.000
Co(II) + buffer + EDTA + BR-PADAP	0.000
Co(II) + buffer + BR-PADAP + EDTA	0.027
Co(II) + buffer + BR-PADAP + Δt + EDTA	0.301

Δt - 30 min

resolves this inconvenience. The effect of the amount of EDTA on the cobalt-Br-PADAP complex was studied and the results show that it can be used as a masking agent, for at least up to 0.080 M (Fig. 3). However, it must be added after the complex formation of Br-PADAP with cobalt. The presence of EDTA does not affect the stability of the system for at least 24 h.

Conditions for the measurement of the first-derivative value

The absorption spectrum and first-derivative spectrum of the cobalt(II)-Br-PADAP complex are shown in Figs. 4 and 5, respectively.

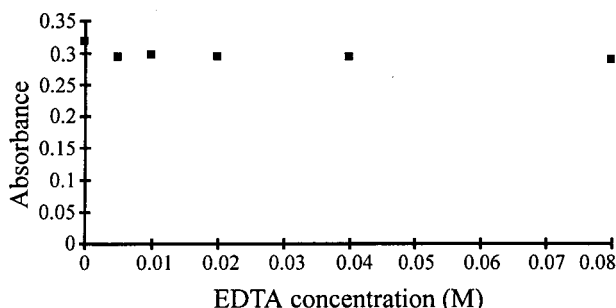


Figure 3. Effect of the EDTA amount on the Co(II)-Br-PADAP system. $[Co^{+2}] = 5.0 \mu g/25.00 \text{ mL}$, $pH = 4.0$.

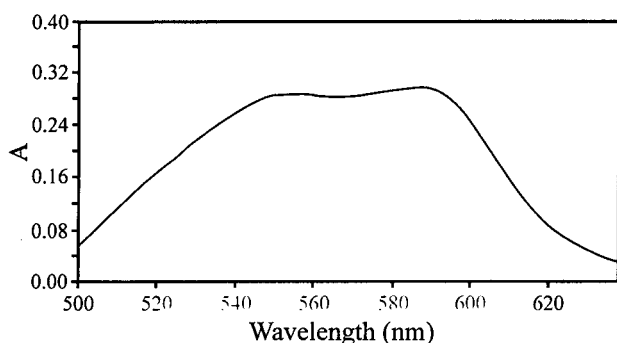


Figure 4. Absorption spectrum of the Co(II)-Br-PADAP complex. $[Co^{+2}] = 5.0 \mu g/25.00 \text{ mL}$, $pH = 4.0$
A Absorbance.

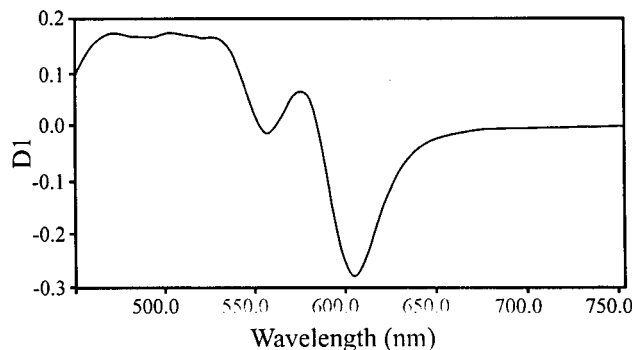


Figure 5. First-derivative spectrum of the Co(II)-Br-PADAP system. $[Co^{+2}] = 5.0 \mu g/25.00 \text{ mL}$, $pH = 4.0$.
 $D1$ -derivativesignal x 10.

The effects of the scan speed and of the slit width (Δl) on the measurement of the first-derivative signal were examined. The results show that scan speed does not affect the value. In this way, a scan speed of 100 nm/min was chosen. It was also found that there is no significant difference in sensitivity among various Δl 's, but the increase of the slit width decreases the noise, hence a slit of 4 nm was selected in the measurements. The decrease of recorder voltage obviously increases the first-derivative signal, but also increases the noise. Thus, the voltage chosen was 5 mV.

The method used for the quantitative evaluation of the derivative spectra signal is classified as the "peak-zero method".

Effect of interfering ions

Solutions containing 1.00 μg of cobalt(II) and various proportions of several cations and anions were prepared, and the proposed procedure was followed, using EDTA as the masking agent.

The interference limit of an ion was attributed to the proportion in which a change of $\pm 2\%$ in absorbances of the chelates were observed. EDTA is very efficient as masking, and only the iron(II) cation presents great interference. High amounts of copper(II) ion can be masked with thio-sulfate²³. The results are listed in Table 3.

The effect of ionic strength on the system is negligible for 0.1 M concentrations of sodium chloride and potassium nitrate.

Application

In the conventional photometric method, Beer's law was obeyed for at least from 0 to 0.80 $\mu g/mL$, and the graph passed through the origin.

The molar absorptivities are $8.30 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ at 589 nm and $7.60 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ at 567 nm. The calibration graph for the derivative method was linear from 6.50 $\mu g/L$ to 0.25 $\mu g/mL$ cobalt concentration.

Table 3. Cobalt determination in the presence of various ions.

Ion	500 x 1	50 x 1	5 x 1	Reagent used
Ca(II)	N	N	N	CaCO ₃ /HCl
Mg(II)	N	N	N	MgCl ₂ .6H ₂ O
Ba(II)	N	N	N	BaCl ₂ .2H ₂ O
Sr(II)	N	N	N	Sr(NO ₃) ₂
Al(III)	I	N	N	Al ₂ (SO ₄) ₃
Mn(II)	I	N	N	MnSO ₄ .6H ₂ O
Bi(III)	I	N	N	Bi(NO ₃) ₃ .5H ₂ O/HCl
Cd(II)	N	N	N	Cd(Ac) .2H ₂ O
Pb(II)	I	N	N	Pb(NO ₃) ₂
Zn(II)	I	N	N	ZnSO ₄ .7H ₂ O
Ni(II)**	I	N	N	NiSO ₄ .7H ₂ O
Hg(II)*	I	N	N	HgO/HNO ₃
Cu(II)*	I	N	N	CuSO ₄ .5H ₂ O
Fe(III)	I	N	N	Fe ₂ (SO ₄) ₃ /HCl
Fe(II)	I	I	I	Fe(III)+ NH ₂ OH.HCl
NO ₃ (I)	N	N	N	NaNO ₃
Cl(I)	N	N	N	NaCl
SO ₄ (II)	N	N	N	Na ₂ SO ₄
CO ₃ (II)	I	N	N	Na ₂ CO ₃
PO ₄ (III)	I	N	N	Na ₃ PO ₄

I = interferences. N = does not interfere [Co]: 1.00 µg/25 mL.

* Can be masked with thiosulfate. ** Amount allowed - 300 µg.

Table 4. Analytical characteristics of the procedures.

	Ordinary spectrophotometric	Derivative spectrophotometric
Molar absorptivity	8.59 x 10 ⁴ L/mol.cm	
Calibration sensitivity	Abs = 1.406.C _{Co} (mg/mL)	H _(cm) = 0.20.C _{Co} (mg/L)
Analytical sensitivity	127.81 mL/µg	1.67 cm/L/µg
Limit of detection (C _L)	2.20 µg/L	1.9 µg/L
Limit of quantification (C _Q)	7.50 µg/L	6.5 µg/L
Linear dynamic range	7.50 µg/L to 0.80 µg/mL	6.50 µg/L to 0.25 µg/mL
Coefficient of variation	1.33%	1.26%

Table 5. Cobalt determination in nickel matrices.

Sample	Ni	Co found, Br-PADAP method	Co found, ICP method
NiCO ₃	49.45 %	0.38 ± 0.01 %	0.38 ± 0.02 %
Ni(NH ₄) ₂ (SO ₄) ₂ .6H ₂ O	14.86 %	0.27 ± 0.01 %	0.28 ± 0.03 %
Ni(NO ₃) ₂ .6H ₂ O	20.19 %	0.24 ± 0.01 %	0.24 ± 0.01 %
NiCl ₂ .6H ₂ O	24.70 %	0.29 ± 0.01 %	0.30 ± 0.01 %
NiCO ₃ *	49.45 %	67.1 ± 5.1 µg/g	62.3 ± 3.0 µg/g
NiCl ₂ .6H ₂ O*	24.70 %	53.1 ± 2.8 µg/g	57.5 ± 3.3 µg/g

* (µg/g salt) derivative method.

The calibration curves were made according to the procedures described in the experimental part.

The analytical sensitivity²⁴, calibration sensitivity²⁴, limit of detection, and limit of quantification²⁵, as well as other analytical characteristics of procedures A and B are summarized in Table 4.

In the determination of cobalt ion in the presence of large amounts of nickel, the absorbance of the system must be read 90 min after the addition of EDTA to guarantee the decomposition of the nickel(II)-Br-PADAP complex.

The procedure was applied for cobalt determination in several nickel matrices. The results are described in Table 5.

The F'test²⁶ was applied to the results obtained with the Br-PADAP and ICP methods, and it revealed that there is no significant difference in the precision of the two methods.

The application of the paired't test²⁶ to the results in Table 5 revealed that there is no significant difference between the ICP methods and the Br-PADAP method in cobalt determination for these matrices at the 95% confidence level.

Conclusions

The results obtained for cobalt by the Br-PADAP and ICP methods were statistically compared by means of the Student t-test and the variance ratio F'test and no significant difference was found.

As a result, the proposed method is highly useful for routine analysis due to its simplicity.

Acknowledgments

The authors acknowledge financial support from CNPq, FINEP and CAPES.

References

1. Stolyarov, K.P.; *Zh. Anal. Khim.* **1961**, *16*, 452; *Anal. Abs.* **1962**, *9*, 1062.
2. Rózycki, C.; *Chemia Analit.*; Warsaw, **1967**, *12*, 131; *Anal. Abs.* **1968**, *75*, 2013.
3. Pontet, M.; *Chim. Anal.* **1955**, *37*, 372; *Anal. Abs.* **1956**, *3*, 2099.
4. Claassen, A.; Daamen, A.; *Anal. Chim. Acta* **1955**, *12*, 547.
5. Flaschka, H.; Speights, R.M.; *Microchem. J.* **1969**, *14*, 490.
6. Ershova, N.S.; Orlov, V.V.; Ivanov, V.M.; Busev, A.I.; *Zavod. Lab.* **1975**, *41*, 913; *Chem. Abs.* **1976**, *84*, 25441s.
7. Goto, H.; Kakita, Y.; Namiki, M.; *J. Jap. Inst. Metals*, **1961**, *25*, 181; *Anal. Abs.* **1962**, *9*, 1918vi.
8. Affsprung, H.E.; Barnes, N.A.; Potratz, H.A.; *Anal. Chem.* **1951**, *23*, 1680.
9. Cheng, K.L.; Warmuth, F.J.; *Chemist-Analyst*, **1959**, *48*, 96.
10. Iida, Y.; Mizuike, A.; Hirano, S.; *J. Chem. Soc. Jap., Ind. Chem Sect.* **1958**, *61*, 1459.
11. Vydra, F.; Markova, V.; *Chemist-Analyst* **1965**, *54*, 69.
12. Luke, C.L.; *Anal. Chem.* **1960**, *32*, 836.
13. Cherepakhin, A.I.; *Zh. Anal. Khim.* **1966**, *21*, 502; *Chem. Abs.* **1966**, *65*, 4648a.
14. Ivanov, V.M.; Busev, I.; Smirnova, L.I.; *Zh. Anal. Khim.* **1970**, *25*, 1149; *Chem. Abs.* **1970**, *73*, 105131d.
15. Klochkovskii, S.P.; Chistota, V.D.; *Zavod. Lab.* **1970**, *36*, 911; *Chem. Abs.* **1971**, *74*, 19024k.
16. Zbíral, J.; Sommer, L.; *Fresenius' J. Anal. Chem.* **1981**, *306*, 129.
17. Huo, K.; *Fenxi Huaxue* **1984**, *12*, 558; *Anal. Abs.* **1985**, *47*, 2B148.
18. Miura, J.; *Analyst* **1989**, *114*, 1323.
19. Ping, X.; *Yankuang Ceshi* **1989**, *8*, 101; *Anal. Abs.* **1990**, *52*, 7B145.
20. Cheng, K.L.; *Handbook of Organic Analytical Reagents*; CRC, Boca Raton, 1982.
21. Lurie, J.; *Handbook of Analytical Chemistry*; MIR, Moscow, 1978.
22. Montaser, A.; Golightly, D.W.; *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*; VCH; New York, 1992.
23. Costa, A.C.S.; Ferreira, S.L.C.; Andrade, M.G.M.; *Talanta* **1993**, *40*, 1267.
24. Skoog, D.A.; Leary, J.J.; *Principles of Instrumental Analysis*; Saunders College; Orlando, 1992.
25. Medinilla, J.; Ales, F.; Garcia Sanchez, F.; *Talanta* **1986**, *33*, 329.
26. Christian, G.; *Analytical Chemistry*; Wiley; New York, 1980.