VERSITA

Cent. Eur. J. Chem. • 8(1) • 2010 • 34–40
DOI: 10.2478/s11532-009-0093-0

Central European Journal of **Chemistry**

Cloud point extraction and preconcentration of gold in geological matrices prior to flame atomic absorption determination

Research Article

Wifky S. El-Naggar[1], Taysseer A. Lasheen[1], El-Said A. Nouh[1]*, Ahmed K. Ghonaim[2]

[1] *Department of Isotopes Geology, Nuclear Materials Authority, El Maadi, P.O. Box 530, Cairo, Egypt*

[2] *Department of Chemistry, Faculty of Science, University of Zagazig, P.O. Box 44519, Zagazig, Egypt*

Received 6 April 2009; Accepted 5 July 2009

Abstract: Brilliant green was used as a complexing agent in cloud point extraction (CPE) and applied for selective preconcentration of trace amounts of gold in geological matrices. The analyte in the initial aqueous solution was acidified with hydrochloric acid (0.1 M) and octylphenoxypolyethoxyethanol (Triton X-114) was added as a surfactant. After phase separation, based on the cloud point separation of the mixture, the surfactant rich phase was diluted with methanol and the analyte determined in the surfactant rich phase by flame atomic absorption spectrometry (FAAS). After optimization of the complexation and extraction conditions, a preconcentration factor of 31 was obtained for only 10 mL of sample. The analytical curve was linear in the range of 3–1000 ng mL^{-1} and the limit of detection was 1.5 ng mL^{-1}. The proposed method was applied to the determination of gold in geological samples..

Keywords: *Gold • Cloud point extraction • Flame atomic absorption spectrometry • Geological samples*

1. Introduction

Gold belongs to the group of elements which occur on the Earth with very low natural abundances. Its concentration is about 4 ng g^{-1} in basic rocks and 1 ng g^{-1} in soils. The values of 0.05 and 0.2 ng mL^{-1} were found in seawater and river water, respectively [1]. As a rule, the direct determination of gold in complex samples containing iron, aluminum, copper, or cobalt by atomic spectrometry is impossible and separation is used [2]. In environmental, geological and biological samples, the low concentration of gold together with the high concentration of interfering matrix components often require an additional enrichment step combined with a matrix separation.

Several analytical techniques such as flame and electrothermal atomic absorption spectrometry (FAAS and ETAAS) [3-8], inductively coupled plasma atomic emission spectrometry (ICP–AES) [9,10], inductively coupled plasma mass spectrometry (ICP–MS) [11,12] and stripping voltammetry [13] have been reported for the determination of gold in different samples. In combination with these techniques, various preconcentration and separation procedures have also been used. These include solvent extraction [14,15], solid phase extraction [16–21], coprecipitation [22] and electrodeposition [23,24].

The classical liquid–liquid extraction and separation methods are usually time consuming and labor intensive and require relatively large volumes of high purity

* *E-mail: saidnouh81@yahoo.com*

solvents. Of additional concern is disposal of the solvent used, which creates a severe environmental problem [25]. Cloud-point extraction is an attractive technique that reduces the consumption of and exposures to solvent, while reducing disposal costs and extraction time [26-33].

Separations and/or preconcentration based on cloud point extraction (CPE) are becoming important and practical applications of surfactants in analytical chemistry [34,35]. This technique is based on the property of most nonionic surfactants in aqueous solutions to form micelles and to separate into a surfactant-rich phase of a small volume and a diluted aqueous phase when heated to a temperature known as the cloud point temperature. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, speedy, and of lower toxicity to the environment than those extractions that use organic solvents. Cloud point methodology has been used to separate and preconcentrate organic compounds as a step prior to their determination in hydrodynamic analytical systems such as liquid chromatography [36] and capillary electrophoresis [37]. The phase separation phenomenon has been also used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes [38,39]. Cloud point extraction as a preconcentration step in conjunction with spectrophotometry, FIA-spectrofluorimetry, FAAS, ETAAS, ICP-AES, and HPLC for the determination of various metal ions has been widely studied [40-45]. CPE combination with FAAS for determination of gold using O,O-diethyldithiophosphate as chelating agent and Triton X-114 as surfactant has also been reported [46]. Gold was preconcentrated mediated by PONPE 7.5 and then determined by ETAAS [47]. PONPE-7.5 requires a lower temperature, around 5ºC for the phase separation. Triton X-114 has a very convenient cloud point, in the range 23-25ºC. Brilliant green which is a basic water-soluble dye has not been used previously in cloud point preconcentation and has the advantage of being stable in acidic solution. The aim of this work was to optimize the use of brilliant green in CPE to assess its application to the preconcentration of gold in geological samples prior to FAAS determination.

2. Experimental

2.1. Reagents

All chemicals and reagents were of analytical grades from Fluka or Merck. A stock solution of 1×10^{-2} mol L^{-1} brilliant green was prepared by dissolving appropriate amounts of this reagent in doubly distilled water. Working standard solutions were obtained by appropriate dilution of the stock standard solutions with methanol (Adwic). The glass vessels used for trace analysis were precleaned by soaking in a sulfochromic acid mixture and subsequently rinsed 3 times with doubly distilled water before use.

2.2.Apparatus

A Thermo Electron Corporation- S series Atomic Absorption Spectrometer with deuterium lamp background correction and a gold hollow cathode lamp (current, 15 mA and slit width, 0.5 nm) was used for gold determination at 242.2 nm. The operating conditions were those recommended by the manufacturer, unless specified otherwise. The sample and the acetylene flow rates and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution in methanol. Cloud point preconcentration experiments were performed using a thermostatic water bath (Büchi 462), maintained at the desired temperature and phase separation was assisted using a centrifuge (Janetzki T32c).

2.3. Cloud point extraction procedure

Aliquots of 10.0 mL of the sample or standard solution containing the analyte (3-200 ng mL^{-1}), Triton X-114 (0.05% (v/v)), brilliant green (5×10^{-5} mol L^{-1}) and hydrochloric acid (0.1 mol L^{-1}), were kept in a thermostated bath at 50ºC for 10 min. Separation of the aqueous and surfactant-rich phases was accomplished by centrifugation for 10 min at 3500 rpm. After cooling in an ice acetone mixture the aqueous phase was then easily removed by decantation. To decrease the viscosity of the surfactant rich phase and facilitate sample handling, 200 µL of methanol was added. The resultant solution was introduced into the FAAS by conventional aspiration.

2.4. Samples analysis

Three certified reference geological materials of granite type having an average oxides of [SiO_2 (72.5%), Al_2O_3 (12.8%), TiO_2 (0.15%), Fe_2O_3 (4.08%), FeO (0.2%), MnO (0.002%), MgO (1.2%), CaO (0.05%), Na_2O (3.3%), K_2O (5.07%), P_2O_5 (0.04%), L.O.I (0.75%), total (100.16%)], namely: ST04/8193, ST06/0250 and ST16/1291 were obtained from Gannet Factory, Australia [48]. Also, five silicate rock samples with average oxides of [(SiO_2 (72%), Al_2O_3 (10%), TiO_2 (0.29%), Fe_2O_3 (9.17%), FeO (0.27%), MnO (0.12%), MgO (1.15%), CaO (0.64%), Na_2O (1.5%), K_2O (2.07%), P_2O_5 (0.98%), L.O.I (1.98%), Total (100.17%)] were collected from the El-Sukkary

area, Egypt and were determined by ICP-MS (ACME Labs. Canada) using geochemical ultra trace aqua regia digestion method.

Each rock sample was grinded, homogenated and quartered.A representative sample was then grinded to -200 mesh. The samples were dried overnight at 80°C.

5 g of each sample was weighed and digested in aqua regia by stirring on a hot plate at 50°C for four hours. After cooling, the solution of each sample was centrifuged and filtered. The filtered solution was diluted with distilled water up to 100 mL. Finally, 5.0 mL of this solution was poured into Falcon tubes and after addition of Triton X-114 and brilliant green the volume was adjusted to 10 mL containing 0.1 M hydrochloric acid. The solution was then extracted using the proposed method at the optimal conditions.

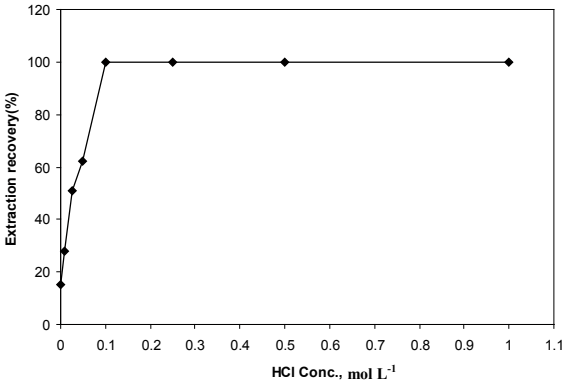

Figure. 1. Effect of HCl concentration on the extraction recovery of Au (100 ng mL^{-1}). 5×10^{-6} mol L^{-1} brilliant green, 0.05% (v/v) Triton X-114.

3. Results and Discussion

3.1. Optimization of variables

3.1.1. Effect of hydrochloric acid concentration

Cloud point extraction of Au was performed using different concentrations, from 0.001 to 1.0 mol L^{-1} of hydrochloric acid since the complexation is more efficient for this analyte in this medium. The effect of hydrochloric acid concentration on Au recovery is depicted in Fig. 1. The extraction yield increases up to a hydrochloric acid concentration of 0.1 mol L^{-1}, reaching a plateau, which was considered as 100% extraction. Hence, a concentration of 0.1 mol L^{-1} hydrochloric acid was chosen for the subsequent experiments.

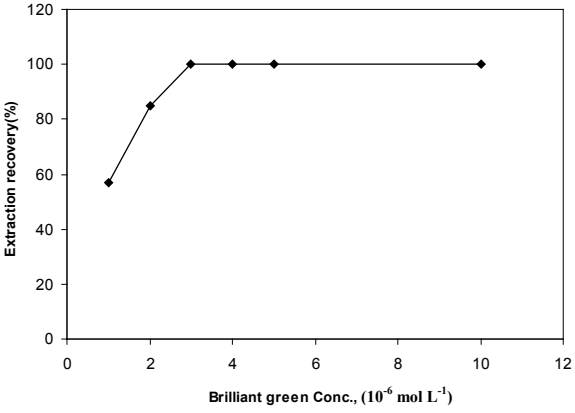

Figure 2. Effect of brilliant green concentration on the extraction recovery of of Au (100 ng mL^{-1}), 0.05% (v/v) Triton X-114, 0.1 M hydrochloric acid.

3.1.2. Effect of brilliant green concentration

The extraction recovery as a function of the brilliant green concentration is shown in Fig. 2. For this study, 10 mL aliquots of a solution containing 100 ng mL^{-1} Au, 0.05% (v/v) Triton X-114 and 0.1 mol L^{-1} hydrochloric acid plus various amounts of brilliant green were subjected to the cloud point preconcentration process. At this stated concentration of gold, ~100% extraction was achieved for a brilliant green concentration of 3×10^{-6} mol L^{-1}. A concentration of 5×10^{-6} mol L^{-1} of brilliant green was chosen for subsequent experiments.

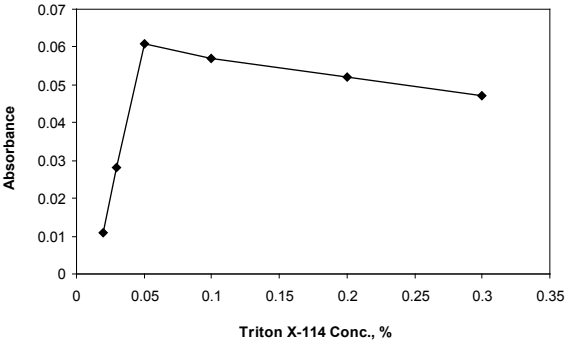

Figure. 3. Variation of the analytical signal of the gold as a function of Triton X-114 concentration Conditions: 100 ng mL^{-1} Au, 5×10^{-6} mol L^{-1} brilliant green, 0.1 M hydrochloric acid.

3.1.3. Effect of Triton X-114 concentration

Triton X-114 was chosen for the extraction due to its low cloud point temperature and high density of the surfactant rich phase; this facilitates phase separation by centrifugation. A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio (*V*org/*V*aqueous), thus improving its concentration ability. The variation of extraction efficiency upon the surfactant concentration was examined within the Triton X-114 range from 0.02-0.3% (v/v), Fig. 3.

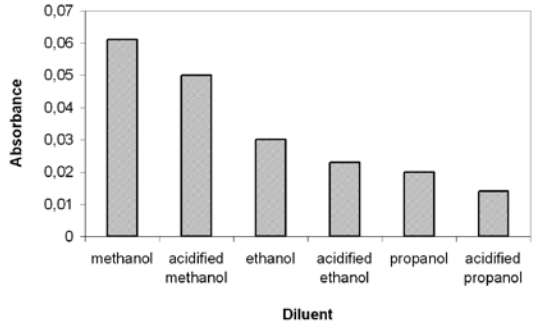

Figure 4. Effect of different diluents on the analytical signal of gold after its separation by CPE. Conditions: 100 ng mL^{-1} Au, 5×10^{-6} mol L^{-1} brilliant green, 0.05% (v/v) Triton X-114, 0.1 M hydrochloric acid

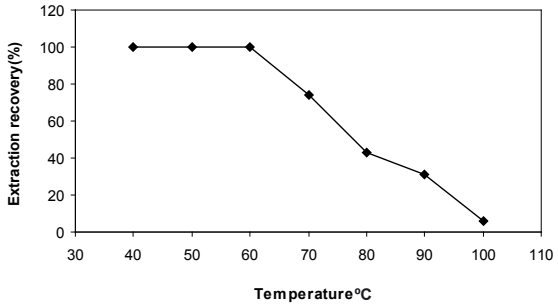

Figure 5. Effect of equilibration temperature on the extraction recovery of Au. Conditions: 100 ng mL^{-1} Au, 5×10^{-6} mol L^{-1} brilliant green, 0.05% (v/v) Triton X-114, 0.1 M hydrochloric acid.

Triton X-114 was found to quantitatively extract the Au– brilliant green complex from aqueous samples at surfactant concentrations of 0.05%, using a single step extraction procedure. Larger quantities of the surfactant can be used at the expense of detection limits, as higher concentrations deteriorate the FAAS signal due to the increase in surfactant volume. Above 0.05% surfactant, analytical sensitivity decreased due to dilution of the sample by additional surfactant solution.

3.1.4. Selection of the dilution agent for the surfactant rich phase

In order to facilitate the sample introduction in the FAAS nebulizer, it was necessary to decrease the viscosity of the surfactant-rich phase. The very high viscosity of this phase (~20 cP) can be decreased using diluting agents. Different solvents such as methanol, ethanol, propanol, and acidic solutions of methanol, ethanol and propanol were tried in order to select the one that could best dissolve the surfactant rich phase completely and give the best sensitivity, Fig. 4. All of these solvents dissolved the extracted phase completely. However, the best results were obtained using methanol.

3.1.5. Effect of equilibration temperature and time

The equilibration temperature above the cloud point and the incubation time were also optimized. It was desirable to employ the shortest incubation time and the lowest possible equilibration temperature, without compromising completion of the reaction and efficient separation of the phases. The results illustrated in Fig. 5 show excellent recoveries for equilibration temperatures between 40 and 60ºC. Higher temperatures lead to the decomposition of brilliant green and a consequent reduction of extraction yield. The dependence of extraction efficiency upon incubation time was studied in the range of 5–30 min. An incubation time of 10 min was optimal for quantitative extraction.

3.2. Characteristics of the method

Calibration curves were obtained by preconcentrating 10 mL of standard solutions with Triton X-114. Table 1 features the analytical characteristics of the method. Under the optimal experimental conditions, the calibration curve for gold was linear from 3 to 1000 ng mL^{-1}. The enhancement factor of about 31 obtained by preconcentrating a 10 mL of sample volume can be considered highly satisfactory. The limit of detection was sufficiently low. Further improvement is also feasible, either by preconcentrating larger amounts of the sample solution or diluting the surfactant-rich phase with a smaller volume of methanol.

Table 1. Analytical characteristics of the method

Parameter	Analytical feature
Concentration range (ng mL^{-1})	3-1000
C_o (ng mL^{-1}) for 0.0044 absorbance[a]	5
Slope (m)	1.02
Correlation coefficient (r)	0.9987
R.S.D. (%) (n = 6)[b]	4.36
LOD (ng mL^{-1})[c]	1.5
Enrichment factor[d]	31

[a] *C_o, the characteristic concentration*
[b] *Gold concentration was 40 ng mL^{-1} for which the R.S.D. was obtained.*
[c] *Limit of detection. Calculated as [(3S.D. of blank /m].*
[d] *Calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration.*

3.3. Interferences

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. The results are shown in Table 2 and prove that Au recoveries are almost quantitative in the presences of interfering cations. Table 3 indicates that the proposed method provides a lower limit of detection than other existing methods [49-55].

Table 2. Effects of the foreign on the recovery of 100 ng mL^{-1} of Au from aqueous solutions

Ion	Concentration (μg mL^{-1})	Ion/Au ratio (w/w)	Recovery (%)
Ca^{+2}	120	1200	103
Mg^{+2}	120	800	102
Na^{+1}	120	800	98
K^{+1}	120	800	102
Al^{+3}	120	800	96
Fe^{+3}	80	800	98
Pb^{+2}	80	800	98
Zn^{+2}	80	800	104
Cr^{+3}	80	800	104
Co^{+2}	80	800	96.4
Cu^{+2}	80	800	98.2
Cd^{+2}	80	800	95.3
Ni^{+2}	80	800	100
Mn^{+2}	80	800	100
Ag^{+1}	40	400	100
Pd^{+2}	40	400	102
Pt^{+4}	40	400	100

Table 3. Comparison of the present method with reported methods for the preconcentration of Au

Cheating Agent	Sorbent or Micellar Media	Analytical Method	DL (ppb)	Reference
Ammonium diethyldithiophosphate	Xylene	FAAS	3	49
	Amberlite XAD-16	FAAS	46	50
	Dowex 1X 4	Spectrophotometric	18	20
Diethyldithiocarbamate	$NaBH_4$	FI–CVG–AAS	24	51
Amidinothiourea	Glass bead	FAAS	4.6	52
	Amberlite XAD-16	FAAS	10	53
2-mercaptothiazole	Silica gel	FAAS	10	4
Amidinothioureido-silica gel	TritonX-114	FI-FAAS	13	1
Activated carbon		FAAS	20	54
Yeast mannan	Carbon electrode	AdCSV	~12	55
Brilliant green	TritonX-114	FAAS	1.5	Present work

Table 4. Determination of Au in certified reference samples using the developed procedure using brilliant green as a complexing agent.

Element	Reference material	Certified Conc. (ng g^{-1})	Measured Conc. (ng g^{-1})[a]
Au	ST04/8193	4720±200	4947±138
	ST06/0250	1050±70	1117±29
	ST16/1291	500±30	510±11

[a]*Mean ± standard deviation (n = 3).*

Table 5. Au content of some silicate rock samples determined by the developed procedure using brilliant green as a complexing agent compared with ICP-MS technique.

Rock sample	ICP-MS Conc. (ng g^{-1})	CPE-FAAS Conc. (ng g^{-1})[a]
1	24753.1	25766.6±737
2	7765.3	7233±405
3	5035.2	4946.6±138
4	4007.5	3950±132
5	6742	6846.67±136

[a]*Mean ± standard deviation (n = 3).*

4. Application

In order to confirm the utility of the proposed method, it was applied to the determination of gold in geological matrices. For this purpose, 10 mL of each of the samples were preconcentrated with 0.05% Triton X-114 and a brilliant green concentration of 5×10^{-6} mol L^{-1}. The suggested method is tested by applying it to the analysis of some certified reference silicate samples (ST04/8193, ST06/0250, and ST16/1291). The results of these determinations are given in Table 4. Good agreement between the found results and the certified values indicates the successful application of the present method for simultaneous determination of Au in these real samples.

The gold content in five collected rock samples (El-Sukkary area, Egypt) is determined by the developed method in the present work by CPE-FAAS and compared with that obtained by the ICP-MS technique. The results show good agreement with each other (Table 5).

5. Conclusions

The proposed method offers a simple, sensitive and inexpensive alternative to other separation/preconcentration techniques. Cloud point extraction with Triton X-114 is an easy and practical procedure for the preconcentration and separation of analytes in aqueous solution, allowing the determination, by FAAS, of ppb levels of Au in silicate rock samples after acid dissolution. Problems with the introduction of the surfactant-rich phase, which is highly viscous, into the nebulizer of the spectrometer are circumvented by dilution with methanol. The complexing agent used in this study, brilliant green, has the advantages of being stable in acidic solution and not requiring a buffered solution. Further, it is fairly selective, leading to an effective separation free from interferences for accurate determination of Au.

References

[1] J. Medved, M. Bujdos, P. Matus, J. Kubova, Anal. Bioanal. Chem. 379, 60 (2004)
[2] S.J. Hill, J.B. Dawson, W.J. Price, J. Anal. At. Spectrom. 14, 1245 (1999)
[3] M. Bagheri, M.H. Mashhadizadeh, S. Razee, Talanta 60, 839 (2003)
[4] Q. Pu, P. Liu, Q. Sun, Z. Su, Microchim. Acta 143, 45 (2003)
[5] B. Gong, Y. Liu, T. Lin, Anal. Chim. Acta 362, 247 (1998)
[6] I. Lopez-Garcia, N. Campillo, I. Arnau-Jerez, M. Hernandez-Cordoba, Spectrochim. Acta B 58, 1715 (2003)
[7] H. Ma, X. Fan, H. Zhou, S. Xu, Spectrochim. Acta B 58, 33 (2003)
[8] G. Ertas, Oy. Ataman, Apel. Spectrosc. 58, 1243 (2004)
[9] Y. Wu, Z. Jiang, B. Hu, J. Duan, Talanta 63, 585 (2004)
[10] N.S. Mokgalaka, T. Wondimu, R.I. McCrindle, J. Anal. At. Spectrom. 19, 1493 (2004)
[11] R. Juvonen, T. Lakomaa, L. Soikkeli, Talanta 58, 595 (2002)
[12] A.K. Shibuya, J.E.S. Sarkis, J. Enzweiler, A.P.S. Jorge, A.M.G. Figueiredo, J. Anal. At. Spectrom. 13, 941 (1998)
[13] A.Z. Abu Zuhri, M.M.S. El-Shahawi, M.M. Kamal, Anal. Chim. Acta 282, 133 (1993)
[14] P. Chattopadhyay, B.V. Sahoo, Analyst 117, 1481, (1992)
[15] A.K. Singh, Talanta 43, 1843 (1996)
[16] Y.S. Chung, R.M. Barnes, J. Anal. At. Spectrom. 3, 1079 (1988)
[17] V.L. Dressler, D. Pozebon, A. Curtius, Anal. Chim. Acta 438, 235 (2001)
[18] T. Saitoh, S. Akita, T. Torii, M. Hiraide, J. Chromatogr. A 932, 159 (2001)
[19] I. Matsubara, Y. Takeda, K. Ishida, Anal. Sci. 19, 1427 (2003)
[20] R. Al-Merey, Z. Hariri, J. Abu Hilal, Microchem. J. 75, 169 (2003)
[21] M. Yu, D. Sun, R. Huang, W. Tian, W. Shen, H. Zhang, N. Xu, Anal. Chim. Acta 479, 225 (2003)
[22] T. Itagaki, T. Ashino, K. Takeda, Fresenius J. Anal. Chem. 368, 344 (2000)
[23] J. Komarek, P. Houserova, Spectrochim. Acta B 58, 1525 (2003)
[24] N.M. Najafi, N. Manouchehri, Anal. Bioanal. Chem. 376, 460, (2003)
[25] J.L. Manzoori, G.K. Nezhad, Anal. Chim. Acta 484, 155 (2003)
[26] F. Shemirani, S.D. Abkenar, R.R. Kozani, M.S. Niasari, A.A. Mirroshandel, Can. J. Anal. Sci. Spectro. 49, 31 (2004)
[27] J.L. Manzoori, A.B. Tabrizi, Anal. Chim. Acta 470, 215 (2002)
[28] M.E.F. Laespada, J.L. Peraz Pavon, B.M. Cordero, Analyst 118, 209, (1993)
[29] F. Shemirani, Sh. Dehghan-Abkena, A.A. Mirroshandel, M.S. Salavati Niasavi, R. Rahnama Kozani, Anal. Sci. 19, 1 (2003)
[30] G.D.L. Paleologos, S.M. Tzouwara-Karaynni, M.T. Karayanis, Anal. Chim. Acta 458, 241 (2002)
[31] E.K. Paleologos, C.D. Stalikas, M.I. Karayannis, Analyst 126, 389 (2001)
[32] M.F. Silva, L. Fernandez, R.A. Olsina, D. Stacchiola, Anal. Chim. Acta 342, 229 (1997)
[33] J.L. Manzoori, A.B. Tabrizi, Microchem. J. 72, 1 (2002)
[34] A. Sanz-Medel, M.R. Fernandez de la Campa, E.B. Gonzalez, M.L. Fernandez-Sanchez, Spectrochim. Acta B 54, 251 (1999)
[35] E.K. Paleologos, D.L. Giokas, M.I. Karayannis, Trends Anal. Chem. 24, 426 (2005)

[36] A.E. Fernandez, Z.S. Ferrera, J.J.S. Rodriguez, Analyst 124, 487 (1999)
[37] R. Carabias-Martinez, E. Rodriguez-Gonzalo, J. Dominguez-Alvarez, J. Hernandez-Mendez, Anal. Chem. 71, 2468 (1999)
[38] C.D. Stalikas, Trends Anal. Chem. 21, 343 (2002)
[39] M.D. Bezerra, M.A.Z. Arruda, S.L.C. Ferreira, Appl. Spectrosc. Rev. 40, 269 (2005)
[40] S. Igarashi, K. Endo, Anal. Chim. Acta 320, 133 (1996)
[41] C. Garcia Pinto, J.L. Perez Pavon, B. Moreno Cordero, E. Romero Beato, S. Garcia Sanchez, J. Anal. Atm. Spectrom. 11, 37 (1996)
[42] J.C. Chen, K.C. Teo, Anal. Chim. Acta 450, 215 (2001)
[43] J.R. Chen, S.M. Xiao, X.H. Wu, K.M. Fang, W.H. Liu, Talanta 67, 992, (2005)
[44] J. Li, P. Liang, T.Q. Shi, H.B. Lu, Atom. Spectrosc. 24, 169 (2003)
[45] A.N. Tang, D.Q. Jiang, Y. Jiang, S.W. Wang, X.P. Yan, J. Chromatogr. A 1036, 183 (2004)
[46] M.A.M. Silva, V.L.A. Frescura, F.J.N. Aguilera, A.J. Curtius, J. Anal. At. Spectrom. 13, 1369 (1998)
[47] J.L. Manzoori, H.A. Zadeh, M. Amjadi, J. Microchim. Acta, 159, 71 (2007)
[48] A. Knowles, Reference Certificate No 1Z53-18-07-01, Gannet Holdings PTY Ltd, Australia
[49] E. Carasek, Talanta 51, 173 (2000)
[50] A. Tunçeli, A.R. Turker, Analyst 122, 239 (1997)
[51] X. Du, S. Xu, Fresenius J. Anal. Chem. 370, 1065 (2001)
[52] P. Liu, Q. Pu, Z. Su, J. Anal. Chem. 60, 908 (2005)
[53] L. Elçi, M. Soylak, A. Uzun, E. Büyükpatır, M. Doğan, Fresenius J. Anal. Chem. 368, 358 (2000)
[54] G. Chakrapani, P.L Mahanta, D.S.R. Murty, B. Gomathy, Talanta 53, 1139 (2001)
[55] B. Lacka, J. Duncanb, T. Nyokong, Anal. Chim. Acta 385, 393 (1999)