

Cloud point extraction and flame atomic absorption spectrometric determination of gold and silver in geological samples

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Summary. Cloud point extraction was suggested as a preconcentration step prior to flame atomic absorption spectrometry (FAAS) determination of gold and silver in geological samples. After complexation with 1,5-diphenylthiocarbazone (dithizone), the analytes could be quantitatively extracted into the phase rich in the surfactant octylphenoxypolyethoxyethanol (Triton X-114). After phase separation and dilution of the surfactant-rich phase with methanol, the enriched analytes are determined by FAAS. The parameters affecting the extraction efficiency, such as solution pH, concentration of dithizone and Triton X-114, equilibration temperature and incubation time, were investigated in detail. Under the optimum conditions, preconcentration of 10 ml of sample solution permitted the detection of 1.4 ng mL^{-1} of Au and 0.53 ng mL^{-1} of Ag with enrichment factors of 47.6 and 55.6, respectively. The proposed method was applied to the determination of Au and Ag in acidic solutions of certified reference geological materials and good agreement with the certified values was obtained.

Introduction

Silver and gold are called “precious” metals⁽¹⁾ These metals have interesting physical and chemical properties beside their low abundance in the earth and their high economic value. Noble metals such as gold and silver are from the rarest on earth, and the abundance of the other precious metals such as platinum and palladium is even less than silver and gold in the earth crust⁽²⁾ However, due to the low concentration of these metals and the high concentration of interfering matrix components in most geologic samples, their determination is often a challenging task for analysts. Therefore, a separation or preconcentration step is often necessary for sensitive, accurate and interference-free determination⁽³⁾. Several analytical techniques such as flame and electrothermal atomic absorption spectrometry (FAAS and ETAAS)⁽⁴⁻¹¹⁾, inductively coupled plasma atomic emission spectrometry (ICP-AES)⁽¹²⁻¹⁴⁾, inductively coupled plasma mass

spectrometry (ICP-MS)⁽¹⁵⁾ and stripping voltammetry⁽¹⁶⁾ have been reported for the determination of gold and silver in different types of samples. In combination with these techniques, various preconcentration and separation procedures have also been used. These include solvent extraction⁽¹⁷⁾, solid phase extraction⁽¹⁸⁻²⁰⁾, coprecipitation^(21,22) and electrodeposition⁽²³⁾.

Solvent extraction is widely used technique, but it has disadvantages such as laborious manipulation and the possibility of emulsion formation. Solid phase extraction using chelating resins as sorbents has also been used extensively. However, quantitative recovery of gold is often difficult due to the strong complexation of gold with functional groups of the resins. The usual method to overcome this problem is the ignition of resin or its treatment with a mixture of inorganic acids. Cloud point extraction (CPE) is a simple and powerful technique for separating and preconcentrating metal ions⁽²⁴⁻²⁷⁾ that can easily be adapted to AAS in order to improve the detection limit and selectivity of determinations. This method has been applied to gold and silver preconcentration using diethyldithiophosphate as chelating agent and Triton X-114 as surfactant prior to its determination by FAAS and ICP-MS^(28,29). Gold and silver were preconcentrated mediated by polyethyleneglycolmono-*p*-nonyphenylether (PONPE 7.5) and then determined by ETAAS^(30,31). The cloud point extraction method has been also applied for silver preconcentration by using dithizone⁽³²⁾ as chelating agent and Triton X-114 as surfactant prior to its determination by FAAS. In the present paper, we have developed and optimized a simple and powerful combined CPE-FAAS methodology for gold and silver determination in geological samples from El-Sukkary area, Egypt. Gold and silver were preconcentrated and mediated by Triton-X114 in the presence of dithizone, and then determined by FAAS.

Experimental

Apparatus

A Thermo Electron Corporation S-series Atomic Absorption Spectrometer with deuterium lamp background correction was used. A gold hollow cathode lamp (current, 10 mA) and slit width, 0.5 nm was used for gold determination at wavelength of 242.8 nm. A silver hollow cathode lamp (current, 4 mA) and slit width, 0.5 nm was used for silver determination at wavelength of 328.1 nm. 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 thermostated bath (Büchi 462), maintained at the desired temperature and phase separation was assisted using a centrifuge (Janetzki T32c).

Reagents

The following reagents were used: Triton X-114 from Fluka was used without further purification. Stock standard solutions of Au and Ag at a concentration $1000 \mu\text{g mL}^{-1}$ were obtained from Merck and Hydrochloric acid from Chem. Loba. A solution of $1 \times 10^{-3} \text{ mol L}^{-1}$ dithizone (Acros Organics) was prepared by dissolving appropriate amounts of this reagent in ethanol. Working standard solutions were obtained by appropriate dilution of the stock standard solutions with methanol (Adwic).

Sample preparation

Each rock sample was ground to -200 mesh and quartered to obtain a representative sample. The samples were dried overnight at 80°C then 5 g of each sample were weighed and digested in aqua regia (80 mL) 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 adjustment

of pH to 4, the volume of solution was adjusted to 10 mL. The solution was then extracted using the proposed method at the optimal conditions. Three certified reference geological materials namely: ST04/8193 (4720 ng mL⁻¹ Au), ST06/0250 (1050 ng mL⁻¹ Au) and ST16/1291 (500 ng mL⁻¹ Au)⁽³³⁾ were analysed. Also, five geological samples collected from El-Sukkary area, Egypt, were analysed by ICP-MS (ACMA lab. Canada) and the results were compared with those obtained by the developed method.

Cloud point extraction procedure

For the CPE, aliquots of 10 mL solution containing 1-200, 1-100 ng mL⁻¹ of Au and Ag respectively, 0.05% Triton X-114 and 1×10^{-5} mol L⁻¹ dithizone adjusted at pH 4 were kept for 15 min in the thermostatic bath maintained at 40 °C. Since the surfactant density is 1.37 g mL⁻¹, therefore, the surfactant-rich phase can settle through the aqueous phase. The phase separation is accelerated by centrifuging at 3000 rpm for 10 min. On cooling in an ice-bath, the surfactant-rich phase became viscous and was retained at the bottom of the tubes. The aqueous phases can readily be discarded simply by inverting the tubes. Later, in order to decrease the viscosity and facilitate sample handling prior to the FAAS assay, 200 µL of methanol solution was added to the surfactant-rich phase. The viscous phase reverted to its normal fluidity. The final solution in methanol was introduced into the nebulizer of the spectrometer by conventional aspiration.

Results and Discussion

Optimization of variables

Effect of pH

Separation of metal ions by cloud point method involves the prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase. CPE of gold and silver was performed in solutions of pH ranging from 1 to 12. The effect of pH on the extraction of gold

and silver complexes is presented in Fig. 1. It clearly shows that the extraction yield depends on the pH at which complex formation occurs. It was found that for silver in the pH range 1–5 and gold in the range 4–12, extraction was quantitative. Hence, a middle range of pH 4 was chosen for these analytes.

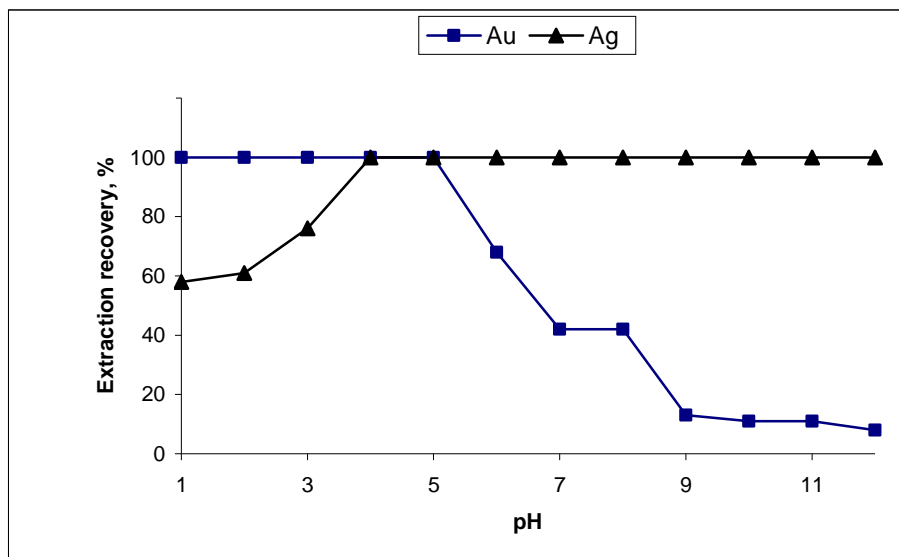


Fig. 1. Effect of pH on the extraction of gold and silver. Conditions: 100 ng mL^{-1} Au, 50 ng mL^{-1} Ag, $1 \times 10^{-5} \text{ mol L}^{-1}$ dithizone and 0.05% (v/v) Triton X-114.

Effect of dithizone concentration

The effect of ligand concentration on the CPE of Au and Ag is given in Fig. 2. In the present study the effect of the ligand concentration was tested in the range of 1×10^{-6} – $2 \times 10^{-5} \text{ mol L}^{-1}$ dithizone. Maximum extraction efficiency was obtained at the concentration of 1×10^{-5} and $5 \times 10^{-6} \text{ mol L}^{-1}$ of dithizone for gold and silver respectively.

Effect of Triton X-114 concentration

A successful cloud point extraction should be able to maximize the extraction efficiency through minimizing the phase volume ratio ($V_{\text{org}}/V_{\text{aqueous}}$), so

as to improve the preconcentration factor. Triton X-114 was chosen as the nonionic surfactant due to its low cloud point temperature, low toxicological properties and cost. Also, the high density of the surfactant-rich phase facilitates phase separation by centrifugation. Triton X-114 was found to quantitatively extract the Au and Ag-dithizone complexes from the aqueous sample solutions at surfactant concentrations above 0.04%, using a single step extraction procedure. Using more than 0.05% of surfactant, the analytical sensitivity decreased due to dilution of the sample by additional surfactant solution.

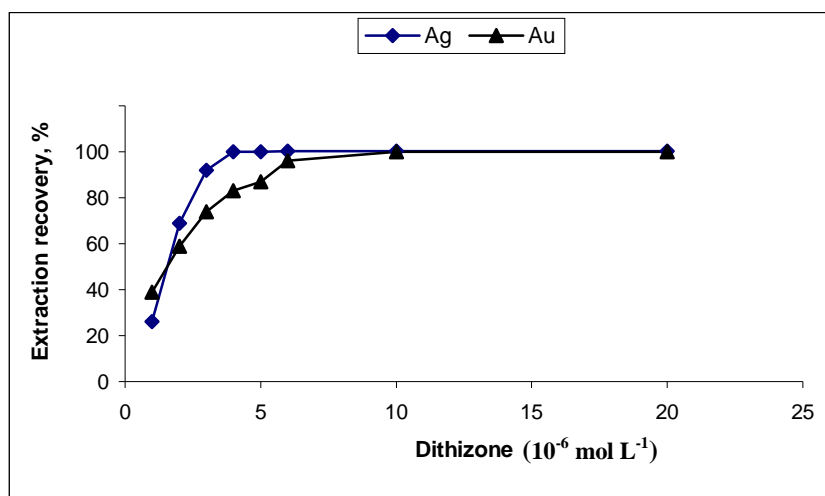


Fig. 2. Effect of dithizone concentration on the extraction of gold and silver. Conditions: 100 ng mL^{-1} Au, 50 ng mL^{-1} Ag, pH 4 and 0.05% (v/v) Triton X-114.

Effect of ethanol concentration

It was found that the absorbance decreased above ethanol concentration of 2% due to dissolution of the surfactant phase and decreasing the volume of this phase. Hence, a relatively concentrated solution ($1 \times 10^{-3} \text{ mol L}^{-1}$) of dithizone in ethanol was used as a standard solution of complexing agent to decrease the concentration of ethanol in experimental solutions.

Selection of the dilution agent for the surfactant-rich phase

Since the surfactant-rich phase obtained after CPE is rather viscous, for the sample introduction in the FAAS nebulizer, it was necessary to decrease the surfactant-rich viscosity. Several synthetic mixtures of varying composition with respect to organic solvents and their acid mixtures were investigated, taking into account that these solvents increase the analytical signal of the FAAS. Solvents tested include methanol, ethanol, propanol, tetrahydrofuran (THF), H₂O and acidic solutions of methanol containing 0.1 M HNO₃, ethanol and propanol. Best results were obtained using methanol, Fig. 3.

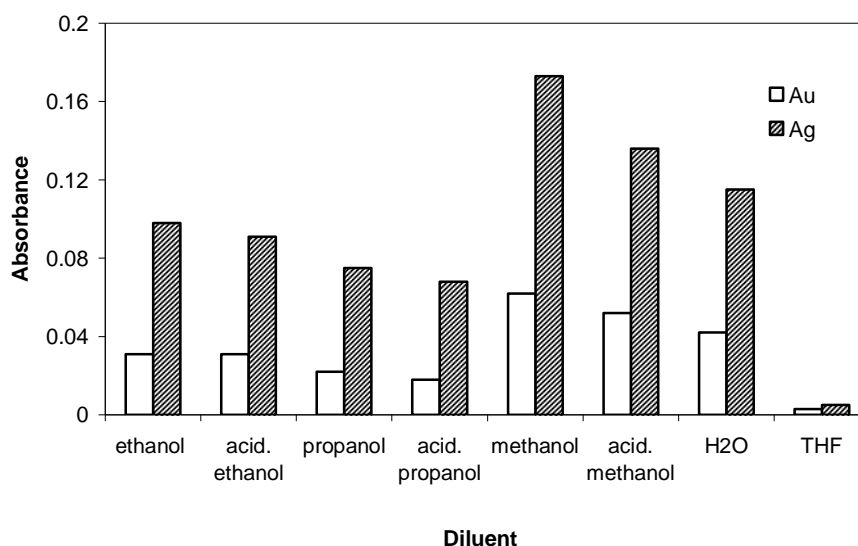


Fig. 3. Effect of various diluents on the analytical signal of gold and silver. Conditions: 100 ng ml⁻¹ Au, 50 ng ml⁻¹ Ag, pH 4, 1×10⁻⁵ mol L⁻¹ dithizone and 0.05% (v/v) Triton X-114.

Effect of viscosity on the analytical signal

After phase separation and removal of aqueous phase, the organic phase is rather viscous so methanol was added to dissolve the organic phase. It was found that for smaller added volumes of methanol, the sensitivity was very high, whereas for higher volumes, there was a decrease in the signal due to dilution. A volume

100 μL gives the best sensitivity; however it shows poor reproducibility, a phenomenon also observed by Shermirani, et al⁽³⁴⁾. So a volume of 200 μL methanol was chosen to be added to the surfactant rich phase to ensure good nebulization of the sample.

Incubation time and equilibration temperature

Optimal incubation time and equilibration temperature are necessary to complete reactions, and to achieve easy phase separation and preconcentration as efficient as possible. It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, a compromise between completion of extraction and efficient separation of the phases. The dependence of absorbance upon equilibration temperature was studied within the temperature range 40-100 $^{\circ}\text{C}$. The results show that the temperature has no significance effect on gold and silver absorbance. A temperature of 40 $^{\circ}\text{C}$ was hence used in all experiments. The dependence of absorbance on equilibration time was studied for a time span of 5-25 min. An equilibration time of 10 min was chosen to be the optimal time to achieve quantitative extraction.

Analytical characteristics

Calibration graphs were obtained by preconcentrating 10 mL of standard solution in the presence of 0.05% Triton X-114 in a medium buffered at pH 4. A volume of 200 μL of the final solution was introduced into the flame by conventional aspiration via the sample aspiration tubing. In this case, linear relationships between the absorbance measured and the concentration of metal prepared for the calibration solution were obtained. Table 1 gives the calibration parameters, the relative standard deviation obtained for 6 analyte samples subjected to the complete procedure and the detection limits. Preconcentration of only 10 mL of sample in the presence of 0.05% Triton X-114 permitted the detection of 1.4 and 0.53 ng mL^{-1} for gold and silver respectively. The

preconcentration factors calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration were 47.5 and 55.6 for gold and silver, respectively. Table (1) summarizes the analytical characteristics of CPE method.

Table 1: Analytical characteristics of the method

Parameter	Au	Ag
Linear range (ng mL ⁻¹)	1-200	1-100
C ₀ (ng mL ⁻¹) ^a	2.3	0.44
Slope (<i>m</i>) (10 ⁻³)	1.91	9.993
Correlation coefficient (<i>r</i>)	0.999	0.9994
R.S.D. (%) (<i>n</i> = 6) ^b	4.9	3.8
LOD(ng mL ⁻¹) ^c	1.4	0.53
Enrichment factor ^d	47.5	55.6

^a C₀, the characteristic concentration for 0.0044 absorbance

^b Gold and silver concentrations were 40 ng mL⁻¹ and 10 ng mL⁻¹, respectively for which the R.S.D. was obtained.

^c Limit of detection. Calculated as $[(3S.D. \text{ of blank } / m)]^{(47)}$.

^d Calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration.

Interferences

In the view of the high selectivity provided by FAAS, the only interferences studied were those related to the preconcentration step. Cations that may react with dithiazone and extracted to the surfactant rich phase were studied. The results shown in table 2 reveal that gold and silver, recoveries were nearly quantitative in the presence of other cations. However, Cu decreases the response. The extraction efficiency of gold is decreased by increasing Cu concentrations. This behavior is attributed to Cu(II) which, consuming the ligand (dithizone). Copper interference is removed by using 0.1 mol L⁻¹ ascorbic acid as reducing agent. The dithizone does not complex Cu (I), which is then separated by the proposed procedure (CPE).

Table 2: Effects of other cations on the extraction of 20 ng mL⁻¹ of Au and 10 ng mL⁻¹ of Ag from aqueous solutions.

Ion	Ion/Au ratio (w/w)	Ion/Ag ratio (w/w)	Recovery (%)	
			Au	Ag
Fe ⁺³	500	1000	100	98.5
Pb ⁺²	500	1000	97	100
Zn ⁺²	500	1000	98	99.5
Cr ⁺³	500	1000	97	97.5
Co ⁺²	500	1000	100	97.4
^a Cu ⁺²	500	1000	100	97.4
Cd ⁺²	500	1000	97	97.4
Ni ⁺²	500	1000	97	100
Mn ⁺²	500	1000	100	98.5

^a 0.1 mol L⁻¹ ascorbic acid is added

Determination of Au and Ag in geological samples

In order to confirm the usefulness of the proposed method, it was applied to the determination of gold and silver in geological samples. For this purpose, 10 ml of each of the samples were preconcentrated with 0.05% Triton X-114 and a dithizone concentration of 1×10^{-5} mol L⁻¹. The proposed method was tested by applying the present method for the analysis of some certified reference samples (ST04/8193, ST06/0250, and ST16/1291) (Gannet Factory, Australia),⁽³³⁾. The results of these determinations (3 determinations for each one) are given in table (3). Good agreement between the found results and certified values indicates the successful applicability of the present method for direct determination of Au in the reference samples.

To evaluate the applicability of the method for Au and Ag elements in collected samples (El-Sukkary area, Egypt), five samples were analyzed. The gold and silver contents were determined by the developed method, CPE-FAAS and then the results were compared with that obtained by the ICP-MS technique. The results of Au and Ag obtained showed good agreement with that obtained by ICP-MS as illustrated in tables (4). Tables 5, 6 indicate that the proposed method is accurate, faster and simpler than the existing methods and it provides lower limit of detection.

Table 3: Determination of Au in certified reference samples by the developed procedure using dithizone as a complexing agent.

Element	Reference material	Certified Conc.($\mu\text{g g}^{-1}$)	Measured Conc.($\mu\text{g g}^{-1}$)	RSD%
Au	ST04/8193	4.720	5.046	1.09
	ST06/0250	1.050	1.050	4.7
	ST16/1291	0.500	0.494	4.2

Table 4: Gold and silver contents of some rock samples (El-Sukkary area, Egypt) determined by the developed procedure using CPE - FAAS compared with ICP-MS technique.

Rock sample	ICP-MS Conc.($\mu\text{g g}^{-1}$)		CPE-FAAS Conc.($\mu\text{g g}^{-1}$)		RSD%	
	Au	Ag	Au	Ag	Au	Ag
	1	24.753	5.948	24.000	5.889	2.5
2	7.765	5.953	7.500	5.910	6.6	1.1
3	5.035	<0.27	5.046	<0.27	2.7	-
4	4.007	1.867	4.038	1.869	3.3	0.5
5	6.742	1.393	6.715	1.376	0.4	1.8

Table 5: Comparison of the present method with the reported methods for the preconcentration and determination of Au

Cheating Agent	Sorbent Or Micellar Media	Analytical Method	DL ($\mu\text{g L}^{-1}$)	Ref.
Ammonium diethyldithiophosphate	xylene	FAAS	3	35
	Amberlite XAD-16 resin	FAAS	46	36
	Dowex 1X 4	Spectrophotometric	18	18
diethyldithiocarbamate	Duolite GT-73 resin	ICP-ES	0.085	37
	NaBH ₄ in acidified immobilized glass bead	FI-CVG-AAS	24	38
Amidinothiourea	Amberlite XAD-16	FAAS	4.6	39
	immobilized silica gel	FAAS	10	40
2-mercaptothiazole	immobilized silica gel	FAAS	10	41
Amidinothioureido-silica gel activated carbon	TritonX-114	FI-FAAS	13	42
		FAAS	20	43
yeast mannan	A glassy carbon electrode	AdCSV.	~12	44
1,8-diamino-4,5-dihydroxy anthraquinone	TritonX-114	ICP-OES	0.5	45
Dithizone	TritonX-114	FAAS	1.25	Present work

DL detection limit ($\mu\text{g L}^{-1}$)

Table 6: Comparison of the present method with the reported methods for the preconcentration and determination of Ag

Cheating Agent	Sorbent Or Micellar Media	Analytical Method	DL. ($\mu\text{g L}^{-1}$)	Ref.
Dicyclohexano-18-crown-6	1,2-dichloroethane	FAAS	13	46
5-(<i>p</i> -dimethylaminobenzylidene) rhodanine	a polystyrene–divinylbenzene disk	diffuse reflectance spectroscopy (DRS)	~4	47
<i>o,o</i> -diethyldithiophosphate	Triton X-114	FAAS	0.46	28
bis(2-mercaptoanil) Acetylacetone	Triton X-114	FAAS	0.43	48
Amidinothioureido-silica gel	TritonX-114	FI-FAAS	1.1	42
Activated carbon		FAAS	7	43
Dithizone	TritonX-114	FAAS	0.27	Present work

Conclusion

In this study, we proposed the use of cloud point extraction as an alternative method for the preconcentration of Au and Ag as a prior step for its determination by FAAS. The method allows the determination of ultra low levels of Au and Ag by FAAS. The methodology offers a simple, rapid, sensitive, low cost, good extraction efficiency and lower toxicity than those methods using organic solvents. The method gives a low limit of detection and good R.S.D. compared with other methods and interference from other cations is minor. The proposed method can be applied for the determination of gold and silver in geological samples.

References

1. F.R. Hartley (Ed.) Chemistry of the Platinum Group Metals, Elsevier, Amsterdam, The Netherlands, (1991)
2. D. J. Bartkowiak, B.N. Kolarz, Eur. Polym. J., 38, 2239,(2002)
3. K. Pyrzyńska, Spectrochim Acta B,60, 1316, (2005)

4. M. Bagheri, M.H. Mashhadizadeh, S. Razee, *Talanta*, 60, 839, (2003)
5. Q. Pu, P. Liu, Q. Sun, Z. Su, *Microchim. Acta*, 143, 45, (2003)
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. J. Medved, M. Bujdos, P. Matus, J. Kubova, *Anal. Bioanal. Chem.*, 379, 60, (2004)
9. G. Ertas, O.Y. Ataman, *Appl. Spectrosc.*, 58, 1243, (2004).
10. J. Šřamková, S. Kotrl'y, P. Jakoubková, *Anal. Chim. Acta*, 408, 183, (2000)
11. M.G. Baron, R.T. Herrin, D. E. Armstrong, *Analyst*, 25, 123, (2000)
12. Y. Wu, Z. Jiang, B. Hu, J. Duan, *Talanta*, 63, 585, (2004)
13. N. S. Mokgalaka, T. Wondimu, R. I. McCrindle, *J. Anal. At. Spectrom.*, 19, 1493, (2004)
14. R.P. Singh, E.R. Pambid, *Analyst*, 115, 301, (1990)
15. K. Ndungu, M.A. Ranville, R.P. Franks, A.R. Flegal, *Mar. Chem.* 98, 109, (2006)
16. A. Z. Abu Zuhri, M. M. S. El-Shahawi, M. M. Kamal, *Anal. Chim. Acta*, 282, 133, (1993)
17. A.R. Ghiasvand, F. Mordadi, H Sharghi, A.R. Hasaninejad, *Anal. Sci.* 21, 387, (2005)
18. R. Al-Merey, Z Hariri, J. Abu Hilal, *Microchem. J.* 75, 169, (2003)
19. S. Dadfarnia, A.M. Haji Shabani, M. Gohari, *Talanta*, 64, 682, (2004)
20. R.K. Katarina, T. Takayanagi, M. Oshima, S. Motomizu, *Anal. Chim. Acta*, 558, 246, (2006)
21. T. Itagaki, T. Ashino and K.Takeda, *Fresenius J. Anal. Chem.*, 368, 344, (2000)
22. O.D. SantAna, A.L.R. Wagener, R.E. Santelli, R.J. Cassella, M. Gallego, M. Valcarcel, *Talanta*, 56, 673, (2002)
23. M.A. Rahman, S. Kaneco, M.N. Amin, T. Suzuki, K. Ohta, *Talanta*, 62, 1047, (2004)
24. J. L. Manzoori, A. Bavili-Tabrizi, *Anal. Chim. Acta*, 470, 215, (2002)
25. J. L. Manzoori, G. Karim-Nezhad, *Anal Chim Acta*, 521, 173, (2004)
26. A. Tang, G. Ding, X. Yan, *Talanta*, 67, 942, (2005)
27. X. Zhu, X. Zhu, B. Wang, *J Anal. At. Spectrom.*, 21, 69, (2006)
28. M.A.M. Silva, V.L.A. Frescura, F. J. N. Aguilera, A.J. Curtius, *J. Anal. At. Spectrom.*, 13, 1369, (1998)

29. M.A.M. Silva, V.L.A. Frescura, A.J. Curtius, *Spectrochim. Acta B*, 55, 801, (2000)
30. J.L. Manzoori, H. A. Zadeh, M. Amjadi, *J. Microchim. Acta*, 159, 71, (2007)
31. J.L. Manzoori, H. A. Zadeh, M. Amjadi, *J. Hazard. Mater.*, 144, 458, (2007)
32. J.L. Manzoori, G. Karim-Nezhad, *Anal. Chim. Acta*, 484, 155, (2003)
33. A. Knowles, Reference Certificate No 1Z53-18-07-01, GANNET HOLDINGS PTY.LTD, Australia.
34. F. Shemirani, S. Dehghan Abkenar, M. Reza Jamali, *Indian J. Chem.*, 44, 1211, (2005)
35. E. Carasek, *Talanta*, 51, 173, (2000)
36. A. Tunçeli, A.R. Turker, *Analyst*, 122, 239, (1997)
37. P. Pohl, B. Prusisz, *Microchim. Acta*, 150, 159, (2005)
38. X. Du, S. Xu, *Fresenius J. Anal. Chem.*, 370, 1065, (2001)
39. P. Liu, Q. Pu, Z. Su, *J. Anal. Chem.*, 60, 908, (2005)
40. L. Elçi, M. Soylak, A. Uzun, E. Büyükpatır, M. Doğan, *Fresenius J. Anal. Chem.*, 368, 358, (2000)
41. Q. Pu, P. Liu, Q. Sun, Z. Su, *Microchim. Acta*, 143, 45, (2003)
42. S. Zhang, Q. Pu, P. Liu, Q. Sun, Z. Su, *Anal. Chim. Acta*, 452, 223, (2002)
43. G. Chakrapani, P.L. Mahanta, D.S.R. Murty, B. Gomathy, *Talanta*, 53, 1139, (2001)
44. B. Lacka, J. Duncanb, T. Nyokong, *Anal. Chim. Acta*, 385, 393, (1999)
45. L. Tavakoli, Y. Yamini, H. Ebrahimzadeh, A. Nezhadali, S. Shariati, F. Nourmohammadiand, (2008), *J. Hazard. Mater.*, 152, 737, (1999)
46. C.T. Camagong, T. Honjo, *Anal. Bioanal. Chem.*, 373, 856, (2002)
47. M.P. Arena, M.D. Porter and J.S. Fritz, *Anal. Chim. Acta*, 482, 197, (2003)
48. F. Shemirani, M. Jamali, R. Kozani, M. Niasari, *J. Anal. Chem.*, 61, 124, (2006)

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