

*Dedicated to Professor Dimče Tošev on the occasion of his 80th birthday***DETERMINATION OF COBALT, NICKEL AND LEAD IN ARSENIC MINERALS BY ZEEMAN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY****Anna Lazaru and Trajče Stafilov****Institute of Chemistry, Faculty of Natural Sciences and Mathematics, The “Sv. Kiril & Metodij” University, P.O. Box 162, MK-1001 Skopje, Republic of Macedonia*

New methods for determination of Co, Ni and Pb in arsenic minerals realgar and orpiment by Zeeman electrothermal atomic absorption spectrometry have been proposed. To eliminate matrix interferences an extraction separation of investigated elements was suggested. Optimal conditions for the extraction separation of Co, Ni and Pb from arsenic were determined. After the dissolution of mineral samples, Co, Ni and Pb were extracted with sodium diethyldithiocarbamate into methylisobutyl ketone from a medium of pH = 6.0 (Co and Ni) and pH = 10 (Pb). High extraction recovery of Co, Ni, and Pb is obtained if the extraction is performed into carbon tetrachloride from a medium of pH = 6. Instrumental conditions (temperature and time) for the determination of Co, Ni and Pb from organic phase by Zeeman electrothermal atomic absorption spectrometry were established. The procedures were verified by method of standard additions and by analyzing referent standard samples. Calibration curves were made using the proposed extraction procedures for standard solutions of Co, Ni and Pb.

Investigated minerals (realgar and orpiment) originate from the Alšar mine, Republic of Macedonia. It was found that the content of Co, Ni and Pb in realgar ranges from 0.1 to 3.2 $\mu\text{g g}^{-1}$ and in orpiment from 0.1 to 5 $\mu\text{g g}^{-1}$. The detection limit for Co, Ni and Pb in arsenic minerals, calculated as 3 standard deviation of the blank, was found to be 2.0 ng g^{-1} .

Key words: cobalt; nickel; lead; determination; realgar; orpiment; Zeeman electrothermal atomic absorption spectrometry; Alšar mine

INTRODUCTION

The mineral lorandite (TlAsS_2) present in the Alšar deposit, Republic of Macedonia, can be used as solar neutrino detector [1] measuring the content of ^{205}Pb isotope produced by the nuclear reaction between solar neutrino and ^{205}Tl accumulated in lorandite [2, 3]. For this purpose, the mineral should be separated without contamination and therefore, knowledge of lorandite and associated mineral chemical composition is very important. The presence of Pb in the minerals indicates a potential target for the generation of ^{205}Pb resulting from natural radioactivity. The most frequently occurring arsenic minerals in the Alšar location associated with lorandite are realgar (As_4S_4) and orpiment (As_2S_3). Investigation of Pb in these minerals can be used as monitors for determining

contribution of background reactions, which originate from natural radioactivity, on condition that they are genetically formed at the same period as the lorandite [4]. The examinations on the other element contents will contribute to obtaining important knowledge of the mine geochemistry and explanation of the background radiation of the location [5].

There are a number of papers concerning of cobalt, nickel and lead determinations in geological samples by ETAAS. Some authors have suggested direct determination of Co [6–10], Ni [7, 11, 12] and Pb [13–20] from the solutions of dissolved samples or by introducing solid samples [21–25]. In a part of presented paper for Co [7, 26–28], for Ni [27–29] or for Pb [27, 28, 30, 31], the results of investigation of matrix interference are given.

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Stafilov *et al.* [31] showed that the arsenic in mass ratio with lead over 5000:1 decrease lead absorbance when examinations are performed by ETAAS. In the case of Co [26] and Ni [29], arsenic had no influence when 1 g of realgar or orpiment samples were dissolved and made to volume of 50 ml with redistilled water into flask. Zelentsova and Yudelevich [32] showed that arsenic in mass concentration below of 20 mg·ml⁻¹ has not influence on the appears of analytical signals of Co and Ni and below of 10 mg·ml⁻¹ for Pb using ETAAS. Also, it was showed [33] that detection limits for Co, Ni and Pb determination in ultrapure arsenic using Zeeman ETAAS are in the order of 10–50 ng·g⁻¹, without the use of preliminary separation or concentration procedures. To overcome interfer-

ences, an addition of different matrix modifier for Co [6, 7] and Ni [7] was suggested. There exist several few methods for separation and extraction of the investigated elements from the matrix before its determination by ETAAS [34–36].

In this paper, new extraction methods for lead, cobalt and nickel by sodium diethyldithiocarbamate (Na-DDTC) in CCl₄ and methylisobutyl ketone (MIBK) from medium of dissolved arsenic minerals are presented. By an intensive testing the optimal conditions for the extraction separation of Co, Ni and Pb from arsenic were obtained and found the possibility of successful extraction of the investigated elements in CCl₄ [37, 38] and in MIBK as a new organic solvent for Co and Ni.

EXPERIMENTAL

Instrumentation

A Varian SpectrAA 640Z Zeeman atomic absorption spectrophotometer equipped with a Varian PSD-100 Autosampler was used. Light sources were cobalt, nickel and lead hollow cathode lamps. Pyrolytically coated graphite tubes were used. The instrumental parameters for determination of Co, Ni and Pb are given in Table 1.

Table 1

Instrumental parameters for determination of Co, Ni and Pb by ETAAS

Parameters	Co	Ni	Pb
Wavelength, nm	240.7	232.0	283.3
Slit, nm	0.2	0.2	0.5
Lamp current, mA	7	4	5
Calibration mode	Peak height		
Background correction	Zeeman		
DRY			
Medium	Inorganic		MIBK/CCl ₄
Element	Co	Ni Pb	Co Ni Pb
Temperature, °C	85; 95; 120		75; 95; 120
Time, s	5; 40; 10		5; 45; 10
Gas flow, L/min	3; 3; 3		3; 3; 3
PYROLYSIS			
Temperature, °C	750	800	400
Time, s	5; 1; 2		400 400 400
Gas flow, L/min	3; 3; 0		5; 20; 2
			3; 3; 0
ATOMIZING			
Temperature, °C	2300	2400	2100
Time, s	1.1; 2	1.1; 2	1; 2
Gas flow, L/min	0; 0		2300 2400 2100
			1.1; 2 1.1; 2 1; 2
			0; 0
CLEAN			
Temperature, °C	2400	2100	2100
Time, s	2		2300 2400 2100
Gas flow, L/min	3		2 2
GAS			3
	Argon		

Reagents and samples

All reagents and standards were of analytical grade. Stock solutions of cobalt, nickel and lead were prepared by dissolving of high-purity CoCl₂·6H₂O, Ni metal and Pb(NO₃)₂. The mass concentrations of elements in these solutions were 1000 mg·l, from which all diluted solutions were prepared. Mineral specimens of realgar and orpiment were taken from the Alšar mine, Crven Dol locality, adit No 21 [39, 40]. Mineral specimens were carefully selected from ore samples using microscope, and then ground to powder.

Procedures

0.1 g of powdered sample was dissolved in 10 ml concentrated HNO₃ and 1 ml of H₂O₂ (30 %). The solution was evaporated almost to dryness. The residue was dissolved in 2 ml concentrated HCl with a minimum of boiling and 13 ml of bidistilled water were added. The solution was filtered and transferred into a separatory funnel.

Extraction with MIBK. The pH value of the solution was adjusted to 6 with NaOH for Co and Ni and 10 for Pb extraction. Then, 5 ml 0.2 % Na-DDTC solution were added and the mixture was shaken for 1 min. After 15 min, 5 ml of the organic solvent MIBK were added. The mixture was shaken for 3 min and Co, Ni and Pb were determined in the organic layer by ETAAS.

Extraction with CCl₄. The pH value of the solution was adjusted to 6. Then, 5 ml of 0.2 % Na-DDTC solution were added and the mixture was

shaken for 1 min. After 15 min, 5 ml CCl_4 were added. The organic layer was separated, evaporated to dryness and the residue dissolved in 2 ml of concentrated HNO_3 and 5 ml bidistilled water. Co,

Ni and Pb were determined by ETAAS using aliquots of 20 mm^3 that were introduced in the graphite furnace.

RESULTS AND DISCUSSION

Previous investigations [2, 4, 5, 26, 29, 41–43] showed very low Co, Ni and Pb content in the investigated minerals. These facts pointed out to the necessity of prior concentration of Co, Ni and Pb and its separation from the arsenic before the determination by ETAAS. Bode [37] found that Co, Ni and Pb could be satisfactorily extracted with Na-DDTC in CCl_4 in pH range of 5–11. Keil [38] showed that lead was successfully extracted with Na-DDTC in CCl_4 in alkaline medium. On the other side, there is data [44] about lead extraction from As(V) in HF- HNO_3 medium in MIBK.

A satisfactory extraction rate of Co, Ni and Pb from dissolved arsenic mineral in hydrochloric acid solution is obtained using Na-DDTC in CCl_4 extraction at pH 6. We also found that this extraction can be performed using MIBK at pH 6 for Co and Ni, and at pH 10 for Pb. It is also found that the determination of investigated elements can be performed after evaporation of organic solvent and dissolution of the residue by nitric acid.

To check whether As coextracted with cobalt, nickel and lead, aliquote of organic layer after extraction by the proposed procedures (with MIBK and CCl_4) were separated, evaporated to dryness and the residue dissolved in 2 ml of concentrated HCl. Using flame AAS, it was found that extracted amount of As can not interfere on Pb determination by ETAAS. For the same reason, samples with equal concentration of examined elements with and without arsenic were prepared. Interferences on the element absorbance were not found.

To verify the method, some samples of realgar and orpiment minerals with standard addition of Co, Ni and Pb, were prepared and treated by using the proposed procedure.

The results given in Table 2 and in Tables 3 show that satisfactory recovery results were obtained.

The determination of Co, Ni and Pb were also performed in reference standards SU-1, SU-1a, and UM-1 (sulfide ore samples) and NR-3 (Cu concentrate). The results of measured and certified values of examined elements for these standard samples are given in Table 4. As it can be seen (Table 4),

the contents for cobalt, nickel and lead obtained using the proposed methods are very close to the certified values.

Table 2

Determination of Co, Ni and Pb in realgar by method of standard additions (in $\mu\text{g}\cdot\text{g}^{-1}$)

Sample	Added	Calculated	Found	Recovery / %
MIBK				
Cobalt				
1	0.00	–	0.13	–
3	6.45	6.58	6.94	105.5
1	0.00	–	0.80	–
2	5.88	6.68	7.12	106.6
Nickel				
1	0.00	–	0.81	–
2	21.50	22.31	21.66	97.1
1	–	–	0.82	–
2	19.59	20.41	19.93	97.6
1	–	–	0.75	–
2	19.72	20.47	20.34	99.4
Lead				
1	–	–	1.02	–
2	10.75	11.77	11.80	100.3
CCl_4				
Cobalt				
1	–	–	0.10	–
2	3.04	3.14	3.08	98.1
3	6.15	6.25	6.27	100.3
1	0.00	–	0.38	–
2	6.52	6.90	6.56	95.1
Nickel				
1	–	–	1.76	–
2	10.52	12.28	12.86	104.7
3	21.03	22.79	22.48	98.6
Lead				
1	–	–	0.29	–
2	10.25	10.54	10.40	98.7
1	–	–	3.16	–
2	5.09	8.25	8.12	98.4
3	10.87	14.03	14.71	104.8

Table 3

Determination of Co, Ni and Pb in orpiment by method of standard additions (in $\mu\text{g}\cdot\text{g}^{-1}$)

Sample	Added	Calculated	Found	Recovery / %
MIBK				
Cobalt				
1	–	–	0.086	–
2	6.28	6.366	6.30	99.0
1	–	–	0.19	–
2	3.16	3.35	3.21	95.8
Nickel				
1	–	–	1.29	–
3	19.78	21.07	20.40	96.8
1	–	–	4.86	–
2	10.36	15.22	14.45	94.9
3	21.98	26.84	25.96	96.7
Lead				
1	–	–	1.66	–
2	5.18	6.84	6.95	101.6
3	10.99	12.65	13.19	104.3
1	–	–	1.74	–
2	10.47	12.21	11.68	95.7
CCl₄				
Cobalt				
1	–	–	1.16	–
3	6.10	7.26	7.72	106.3
1	–	–	0.18	–
2	3.04	3.22	3.35	104.0
3	6.19	6.37	6.67	104.7
Nickel				
1	–	–	1.42	–
2	10.70	12.12	12.50	103.1
3	20.32	21.74	21.76	100.1
Lead				
1	–	–	2.08	–
2	5.07	7.15	6.97	97.5
3	10.31	12.39	12.76	103.0
1	–	–	3.73	–
2	10.30	14.03	14.91	106.3

Table 4

Determination of Co, Ni and Pb in referent standards samples (given in %)

Ref.	Co		Ni		Pb	
Standard	Certified	Found	Certified	Found	Certified	Found
MIBK						
Su-1	0.063	0.084	1.51	1.46	0.01	0.011
Su-1a	0.041	0.040	1.233	1.040	–	–
UM-1	0.035	0.037	0.88	0.95	–	–
NR-3	0.074	0.084	0.04	0.040	–	–
CCl₄						
Su-1	0.063	0.063	1.51	1.36	0.01	0.012
Su-1a	0.041	–	1.233	1.180	–	–
UM-1	0.035	0.036	0.88	1.02	–	–
NR-3	0.074	0.081	0.04	0.040	–	–

Using these methods, Co, Ni and Pb were determined in various samples of the investigated minerals from the Alšar mine (Table 5). It was found that the content of Co, Ni and Pb in realgar ranges from 0.1 to 3.2 $\mu\text{g}\cdot\text{g}^{-1}$ and in orpiment from 0.1 to 5 $\mu\text{g}\cdot\text{g}^{-1}$. These values are in agreement with those obtained for the same minerals by other authors (Table 5), Palme *et al.* [5] and Frantz *et al.* [42] by neutron activation analysis, Todth [2], Boev *et al.* [41] and Frantz *et al.* [42] by mass spectrometry and Stafilov *et al.* [43] obtained by ETAAS.

Table 5

Measured content levels for Co, Ni and Pb in realgar and orpiment from the Alšar mine (given in $\mu\text{g}\cdot\text{g}^{-1}$)

Mineral / Element	Co	Ni	Pb
Realgar	< 0.08 [5]		0.38 [2]
	< 1 [39]	< 10 [5]	1.654 – 6.2 [41]
	< 4.0 [40]	0.754 – 1.763*	2 [39]
	0.103 – 0.80*		0.007 – 0.08 [40] 0.294 – 3.162*
Orpiment	< 0.41 [5]		11.6 [2]
	< 7 [40]	< 30 [5]	5.3 – 9.4 [41]
	0.086 – 1.164*	1.291 – 4.856*	0.8 [39]
			0.072 – 0.41 [40] 1.654 – 3.726*

*This work

Calibration curves for cobalt, nickel and lead were made using the proposed extraction procedures for their standard solutions. The detection

limit for Co, Ni and Pb, calculated as 3 standard deviations of the blank, was found to be $2.0 \text{ ng} \cdot \text{g}^{-1}$.

REFERENCES

- [1] M. S. Freedman, C. Stevens, E. Horwitz, L. Fuchs, L. Lerner, L. Goodman, W. Childs, J. Hessler, *Science*, **193**, 1117 (1976).
- [2] W. Todt, *Nucl. Instr. Meth. Phys. Res.*, **A271**, 251 (1988).
- [3] M. K. Pavićević, *N. Jb. Miner. Abh.*, **167**, 205 (1994).
- [4] M. S. Freedman, *Proc. Conf. on Status and Future of Solar Neutrino Research* (ed. G. Friedlander), Vol. 1, RNL Report 50879, 1978, pp. 313–360.
- [5] H. Palme, M. K. Pavićević, B. Spettel, *Nucl. Instr. Meth. Phys. Res.*, **A271**, 314 (1988).
- [6] J. Komárek, D. Kolčava, L. Sommer, *Collect. Czech. Chem. Commun.*, **45**, 3313 (1980).
- [7] R. Kuroda, T. Nakano, Y. Miura, K. Oguma, *J. Anal. At. Spectrom.*, **1**, 429 (1986).
- [8] J. S. Baros, *Analyst*, **114**, 369 (1989).
- [9] I. D. Zorkin, O. D. Zubova, *Zh. Anal. Khim.*, **45**, 1858 (1990).
- [10] T. Nakamura, H. Oka, S. Hidehiro, J. Sato, *Analyst (London)*, **117**, 131 (1992).
- [11] V. B. Schweizer, *At. Absorpt. Newsl.*, **14**, 137 (1975).
- [12] J. S. Kane, H. Smith, *Geol. Surv. Open-File Rep.*, **81**, 1981
- [13] J. G. T. Regan, J. Waren, *Analyst*, **101**, 220 (1976).
- [14] C. Manning, W. Slavin, *At. Absorpt. Newsl.*, **17**, 43 (1978).
- [15] L. R. Hageman, J. A. Nichols, P. Vismanadham, R. Woodriff, *Anal. Chem.*, **51**, 1406 (1979).
- [16] M. C. Halliday, C. Houghton, J. M. Ottaway, *Anal. Chem. Acta*, **119**, 67 (1980).
- [17] E. M. Sedykh, Yu. I. Belyaev, E. V. Sorokina, *Zh. Anal. Khim.*, **35**, 2162 (1980).
- [18] M. P. Bertenshaw, D. Geltshorpe, K. C. Wheatstone, *Analyst*, **107**, 163 (1982).
- [19] J. S. Baros, *Analyst*, **114**, 369 (1989).
- [20] S. Bektas, S. Akman, *Anal. Sci.*, **6**, 547 (1990).
- [21] N. G. Karamanova, Yu. P. Pogrebnykh, *Zh. Anal. Khim.*, **34**, 213 (1979).
- [22] Z. Grobrenski, R. Lehmann, *At. Spectrosc.*, **4**, 111 (1983).
- [23] W. Schroen, G. Bombach, *Spectrochim. Acta*, **38B**, 1269 (1983).
- [24] K. P. Schmidt, H. Falk, *Spectrochim. Acta*, **42B**, 431 (1987).
- [25] P. Tittarelli, C. Biffi, *Appl. Zeeman Graphite Furn. At. Absorpt. Spectrom. Chem. Lab. Toxicol.*, 1992, p. 79.
- [26] A. Lazaru, T. Stafilov, *Proceedings on XXVI October Conference of Miners and Metallurgists, Donji Milanovac*, 1994, pp. 427–431.
- [27] E. M. Sedykh, Yu. I. Belyaev, E. V. Sorokina, *Zh. Anal. Khim.*, **35**, 2162 (1980).
- [28] E. M. Sedykh, Yu. I. Belyaev, E. V. Sorokina, *Zh. Anal. Khim.*, **35**, 2348 (1980).
- [29] A. Lazaru, T. Stafilov, *Geologica Macedonica*, **7**, 73 (1993).
- [30] M. Tominaga, Y. Umezaki, *Anal. Chim. Acta*, **139**, 279 (1982).
- [31] T. Stafilov, V. Jordanovska, S. Aleksovska, *Bull. Chem. Technol. Macedonia*, **8**, 93 (1990).
- [32] L. V. Zelentsova, I. G. Yudelevich., *Zh. Anal. Khim.*, **38**, 1404 (1983).
- [33] E. Sentimenti, G. Mazzetto, *Appl. Zeeman Graphite Furn. At. Absorpt. Spectrom. Chem. Lab. Toxicol.*, 1992, p. 95.
- [34] G. P. Sighinolfi, S. Gorgoni, A. H. Mohamed, *Geo-stand. Newsl.*, **8**, 25 (1984).
- [35] R. J. Clark, *J. Anal. At. Spectrom.*, **1**, 301 (1986).
- [36] T. Stafilov, S. Aleksovska, V. Jordanovska, *N. Jb. Miner. Abh.*, **167**, 401 (1994).
- [37] H. Bode, *Z. Anal. Chem.*, **143**, 182 (1954).
- [38] R. Keil, *Z. Anal. Chem.*, **229**, 117 (1967).
- [39] S. Janković, *Nucl. Instr. Phys. Res.*, **A271**, 286 (1988).
- [40] B. Boev, R. Stojanov, G. Denkovski, *Geologica Macedonica*, **7**, 35 (1993).
- [41] B. Boev, T. Serafimovski, B. Milosavljević, *Geologica Macedonica*, **7**, 41 (1993).
- [42] E. Frantz, H. Palme, W. Todt, A. El Goresy, M. K. Pavićević, *N. Jb. Miner. Abh.*, **167**, 359 (1994).
- [43] T. Stafilov, V. Jordanovska, S. Aleksovska, *Bull. Chem. Technol. Macedonia*, **9**, 2, 159 (1990).
- [44] M. Ikramuddin, *At. Spectrosc.*, **4**, 101 (1983).

Резиме

ОПРЕДЕЛУВАЊЕ НА КОБАЛТ, НИКЕЛ И ОЛОВО ВО АРСЕНСКИ МИНЕРАЛИ СО ZEEMAN-ОВА ЕЛЕКТРОТЕРМИЧКА АТОМСКА АПСОРПЦИОНА СПЕКТРОМЕТРИЈА

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у. фах 162, МК-1001 Скопје, Република Македонија***Клучни зборови:** кобалт; никел; олово; определување; реалгар; аурипигмент, Zeeman-ова електротермичка атомска апсорпциона спектрометрија; рудник Алшар

Предложен е нов метод за определување на Co, Ni и Pb во арсенски минерали со Zeeman-ова електро-термичка атомска апсорпциона спектрометрија. За елиминација на влијанијата на матриксот е вршена екстракциона сепарација на испитуваните елементи. За таа цел извршени се испитувања за определување на оптималните услови за екстракционото сепарирање на Co, Ni и Pb од арсенот. По растворањето на минералните обрасци се врши екстракција на Co, Ni и Pb со натриум диетилдитиокарбамат при pH = 6 (за Co и Ni), односно pH = 10 (за Pb) во метилизобутил кетон и во јаглерод тетрахлорид при pH = 6. Утврдени се и инструменталните услови (температура и време) за оп-

ределувањето на Co, Ni и Pb во органската фаза со Zeeman-ова атомска апсорпциона спектрометрија. Постапката е проверена со методот на стандардни додатоци и со примена на методот за определување на испитуваните елементи во референтни стандардни обрасци. Испитуваните минерали (реалгар и аурипигмент) потекнуваат од рудникот Алшар, Република Македонија. Најдено е дека содржината на Co, Ni и Pb во реалгар се движи од 0,1 до 3,2 $\mu\text{g g}^{-1}$, а во аурипигмент од 0,1 до 5 $\mu\text{g g}^{-1}$. Границата на детекција за испитуваните елементи во арсенски минерали изнесува 2,0 ng g^{-1} .