

EXTRACTION OF Co, Ni AND Pb IN ARSENIC MINERALS AND THEIR DETERMINATION BY ZEEMAN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Abstract. A method for determination of Co, Ni and Pb in realgar (As_4S_4) and orpiment (As_2S_3) by Zeeman electrothermal atomic absorption spectrometry was proposed. After the dissolution of mineral samples, Co, Ni and Pb were simultaneously extracted as diethyldithiocarbamate complexes into CCl_4 from a medium of pH 6.0. The procedure was verified by the method of standard additions and by analyzing reference material. Investigated minerals originate from Allchar mine, Republic of Macedonia. It was found that the content of Co, Ni and Pb in realgar ranges from 0.1 to 2 $\mu\text{g} \cdot \text{g}^{-1}$ and in orpiment from 0.1 to 5 $\mu\text{g} \cdot \text{g}^{-1}$. The detection limit for Co, Ni and Pb was found to be 2.0 $\text{ng} \cdot \text{g}^{-1}$.

Key words: Determination, cobalt, nickel, lead, realgar, orpiment, Zeeman electrothermal atomic absorption spectrometry

1. Introduction

Electrothermal atomic absorption spectrometry (ETAAS) was widely used for Pb, Co and Ni determinations, but there is little data about the interference of arsenic as a matrix element on determination on these elements. It was found that the arsenic influence on the absorbance of Pb, Co and Ni is present in higher concentrations [1, 2]. Previous investigations showed very low Co, Ni and Pb concentration in the investigated minerals [2-7]. These facts pointed out to the necessity of Co, Ni and Pb concentrating and its separation from the arsenic before the determination by ETAAS.

This paper presents extraction methods for lead, cobalt and nickel by sodium diethyldithiocarbamate (Na-DDTC) in CCl_4 and methylisobutyl ketone (MIBK) from the medium of dissolved arsenic minerals.

2. Experimental

2.1. Instrumentation

A Varian SpectrAA 604Z 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 are given in Table 1.

2.2. Reagents and Samples

All reagents and standards were of an analytical grade. The stock solutions of cobalt, nickel and lead were prepared by dissolving high-purity $CoCl_2$, Ni metal and $Pb(NO_3)_2$. The concentrations of elements in these solutions were 1000 $\text{mg} \cdot \text{dm}^{-3}$, from which all diluted solutions were prepared. Mineral specimens of realgar and orpiment were taken from the Allchar mine, Crven Dol locality, adit No 21. The minerals were carefully hand picked under a microscope from the ore samples where they were found. Mineral samples were ground to a grain size below 0.063 mm by vibration millstone.

Table 1. Instrumental parameters for determination of Co, Ni and Pb by ETAAS

Element	Co			Ni			Pb		
Wavelength, nm	240.7			232.0			283.3		
Spectral bandwidth, nm	0.2			0.2			0.5		
Lamp current, mA	7			4			5		
Calibration mode	Peak height								
Background correction	Zeeman								
DRY									
Medium	Inorganic						MIBK		
Element	Co	Ni	Pb	Co	Ni	Pb	Co	Ni	Pb
Temperature, °C	85; 95; 120			79; 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	400	400	400			
Time, s	5; 1; 2			5; 20; 2					
Gas flow, L/min	3; 3; 0			3; 3; 0					
ATOMIZING									
Temperature, °C	2300	2400	2100	2300	2400	2100			
Time, s	1.1; 2	1.1; 2	1; 2	1.1; 2	1.1; 2	1; 2			
Gas flow, L/min	0; 0			0; 0					
CLEAN									
Temperature, °C	2400	2100	2100	2300	2400	2100			
Time, s	2			2					
Gas flow, L/min	3			3					
GAS	Argon								

2.3. Procedures

0.1 to 0.5 g of the powdered sample was dissolved in 10 cm³ conc. HNO₃ and 1 cm³ of H₂O₂. The solution was almost completely evaporated and the residue was dissolved in 2 cm³ conc. HCl and adding of 13 cm³ of redistilled water. The solution was filtered and transferred into a separatory funnel. The pH value was adjusted to 6. 5 cm³ of Na-DDTC (0.2 %) was added and the mixture was shaken for 1 min. After 15 min, 5 cm³ of CCl₄ were added. The organic layer after extraction was separated, evaporated to dryness and the residue dissolved in 2 cm³ of conc. HNO₃ and 5 cm³ redistill water. Co, Ni and Pb were determined by ETAAS using aliquots of 20 mL that were introduced in the graphite furnace.

3. Results and Discussion

Bode [8] found that Co, Ni and Pb could be satisfactorily extracted with Na-DDTC in CCl₄ in a pH range of 5-11. Keil [9] showed that lead was successfully extracted with Na-DDTC in CCl₄ in alkaline medium. We obtained a satisfactory extraction rate of Co, Ni and Pb from dissolved arsenic mineral solution with Na-DDTC in CCl₄ of pH 6. We also found that this extraction can be made using organic solvent MIBK in pH of 6 for Co and Ni and in pH of 10 for Pb. It was found that the extracted amounts of the As were below level and can be interfered on a Pb determination by ETAAS.

Table 2. Determination of Co, Ni and Pb in realgar by method of standard additions

Sample	$w_M(\text{added})/\mu\text{g}\cdot\text{g}^{-1}$	$w_M(\text{calc.})/\mu\text{g}\cdot\text{g}^{-1}$	$w_M(\text{found})/\mu\text{g}\cdot\text{g}^{-1}$	Recovery/ %
COBALT				
1	-	-	0.103	-
2	3.042	3.145	3.082	95.0
3	6.147	6.250	6.268	98.2
1	0.00	-	0.380	-
2	6.525	6.905	6.560	95.0
NICKEL				
1	-	-	1.763	-
2	10.515	12.278	12.86	104.7
3	21.030	22.793	22.48	98.6
LEAD				
1	-	-	0.294	-
2	10.246	10.540	10.398	98.6
1	0.00	-	3.162	-
2	5.092	8.256	8.125	98.4
3	10.870	14.032	14.715	104.9

Table 3. Determination of Co, Ni and Pb in orpiment by method of standard additions

Sample	$w_M(\text{added})/\mu\text{g}\cdot\text{g}^{-1}$	$w_M(\text{calc.})/\mu\text{g}\cdot\text{g}^{-1}$	$w_M(\text{found})/\mu\text{g}\cdot\text{g}^{-1}$	Recovery/ %
COBALT				
1	-	-	1.164	-
2	3.20	4.401	4.828	95.0
3	6.098	7.299	7.723	105.0
1	0.00	-	0.180	-
2	3.043	3.223	3.349	103.9
3	6.187	6.367	6.675	104.8
NICKEL				
1	-	-	1.419	-
2	10.695	12.114	12.502	103.2
3	20.325	21.744	21.764	100.0
LEAD				
1	-	-	2.083	-
2	5.071	7.154	6.973	97.0
3	10.309	12.383	12.758	103.0
1	-	-	3.726	-
2	10.30	14.026	14.908	106.3

To verify the method, some samples of realgar and orpiment minerals from Alšar mine, with and without standard additions, were prepared and treated by proposed methods and cobalt, nickel and lead were determined by ETAAS. The results (Tables 2 and 3), show that satisfactory recovery results were obtained.

Determination of cobalt, nickel and lead were also performed for referent 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 show that the concentrations for cobalt, nickel and lead are very similar.

Using these methods, cobalt, nickel and lead were determined by ETAAS in different samples of the investigated minerals from the Alšar mine. 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 by other authors [4, 6] by neutron activation analysis, mass spectrometry [5-7] and by ETAAS [3].

Calibration curves for Co, Ni and Pb were made using the proposed extraction procedures. The detection limit for Co, Ni and Pb was found to be 2.0 $\text{ng} \cdot \text{g}^{-1}$.

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Апстракт. Предложена е метода за определување на Co, Ni и Pb во реалгар (As_4S_4) и аурипигмент (As_2S_3) со примена на Zeeman-ова електротермичка атомска апсорпциона спектрометрија. По растворањето на минералните обрасци, Co, Ni и Pb беа истовремено екстрахирани како диетилдитиокарбаматни комплекси во CCl_4 од средина со $\text{pH}=6.0$. Постапката беше потврдена со методата на стандардни додатоци и со анализирање на референтни материјали. Испитуваните минерали се со потекло од рудникот Алшар, Република Македонија. Утврдено е дека содржината на Co, Ni и Pb во реалгарот се движи од 0,1 до 2 $\mu\text{g} \cdot \text{g}^{-1}$, додека во аурипигментот од 0,1 до 5 $\mu\text{g} \cdot \text{g}^{-1}$. Границата на детекција за Co, Ni and Pb изнесува 2,0 $\text{ng} \cdot \text{g}^{-1}$.