

Determination of trace elements in some copper minerals by atomic absorption spectrometry

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Abstract. Various trace elements (cadmium, chromium, cobalt, iron, nickel, manganese, zinc) in some copper minerals are determined by flame (FAAS) and electrothermal atomic absorption spectrometry (ETAAS). To avoid the interference of the matrix element, a method for electrolytic separation of copper is proposed. For the copper minerals containing iron (chalcopyrite) a method for extraction of iron by isoamyl acetate in HCl solution after separation of copper is applied. The procedure is verified by the method of standard additions. The results of the trace elements determination show that satisfactory recoveries are obtained. The determination of investigated elements is also performed for standard reference copper concentrate. The studied minerals: brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$; chalcantite, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; chalcopyrite, CuFeS_2 ; covellite, CuS ; and native Cu originate from various localities in the Republic of Macedonia.

Key words: copper minerals, trace elements, AAS

1. Introduction

Although minerals are naturally occurring inorganic substances, most of them contain extraneous substances. The knowledge about the presence of trace elements in the mineral sample helps to establish the conditions in which these minerals have been formed. Copper minerals are widespread and even modern culture and life is heavily dependent on copper and copper products. Copper ore could be found in large deposits, relatively close to the surface, and amenable to relatively low cost bulk mining methods. The combination of its physical properties, abundance, and low cost make it a valuable commodity. As a mineral, natural copper (native copper) is relatively rare. Most copper in nature is found in minerals associated with sulfur or in the oxidized products of these minerals. Because copper is produced from the ore deposits, it is very important to follow the content of trace elements in its minerals samples.

The flame (FAAS) and electrothermal (ETAAS) atomic absorption spectrometry has proved to be very useful in geological analysis [1]. Many authors suggest direct determination from the obtained solutions [2-5] or, in the cases when the matrix

element is present in higher concentration, matrix modification or separation is suggested [6-14]. In this work, a method for determination of different trace elements (Cd, Co, Cr, Fe, Mn, Ni, Zn) in copper minerals [brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$; chalcantite, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; chalcopyrite, CuFeS_2 ; covellite, CuS ; and native Cu] is proposed using FAAS and ETAAS after an electrolytic separation of copper (and liquid-liquid extraction of iron for chalcopyrite).

2. Experimental

Instrumentation

A Varian SpectrAA-604Z Zeeman atomic absorption spectrometer equipped with a Varian PSD-100 Autosampler, Varian SpectrAA are used. The instrumental parameters for ETAAS determinations are given in Table 1. Fe and Zn and for some samples Mn are determined by FAAS on Thermo Model Solaar 2 atomic absorption spectrometer.

Reagents and samples

All reagents are of analytical grade. Stock solutions of Cd, Co, Cr, Fe, Mn, Ni and Zn are delivered by Solution Plus Inc. (USA) with the concentration of 1 mg mL⁻¹. Samples of copper minerals originate from Sasa (brochantite, chalcopyrite) and Bučim (chalcantite, chalcopyrite, native Cu) mines from the Republic of Macedonia and covellite from Bor, Serbia and Montenegro.

Table 1. Instrumental condition for determination of cadmium, cobalt, chromium, manganese and nickel by ETAAS

Element	Cd	Cr	Co	Ni
Wavelength/nm	228.8	357.9	242.5	232.0
Slit/nm	0.5	0.5	0.2	0.2
Lamp current/mA	4	7	7	7
Calibration mode	Absorption, peak area			
Background corr.	Zeeman			
Drying				
Temperature/°C	95	95	95	95
Ramp time/s	40	40	40	40
Temperature/°C	120	120	120	120
Ramp time/s	10	10	10	10
Pre-treatment				
Temperature/°C	250	1000	750	800
Ramp time/s	5	5	5	5
Hold time/s	20	20	20	20
Atomization				
Temperature/°C	1800	2600	2300	2400
Ramp time/s	1	1	1	1
Hold time/s	2	2	2	2
Cleaning				
Temperature/°C	2600	2600	2600	2600

Sample preparation

Brochantite and chalcantite. Powdered sample (0.05 to 0.5 g) is dissolved in 10 mL redistilled water in 250 mL glass beaker, additional 90 mL redistilled water are added and 2 mL of conc. H₂SO₄ and 1 mL conc. HNO₃. The Pt-electrode is employed for copper electrolysis for 45 min at 2 V and 3-4 A. After washing the Pt-electrode with redistilled water, copper is dissolved with HNO₃ (1+2) and determined by mass difference. The solution is evaporated to 15-20 ml, transferred into a 25 mL volumetric flask, fill up to the mark, and taken for AAS measurements.

Covellite. Powdered sample (0.05 to 0.5 g) is dissolved in 6 mL of conc. HCl, 2 mL conc. HNO₃ and few drops of conc. H₂O₂. The solution is evaporated to dryness and the residue dissolved in 2 mL of conc. H₂SO₄ and 1 mL conc. HNO₃. The same procedure is carried out as for brochantite.

Native Cu. natural sample (0.05 to 0.5 g) was dissolved in 2 mL of conc. HNO₃. The same procedure is carried out as for covellite.

Chalcopyrite. Powdered sample (0.05 to 0.5 g) was dissolved in 6 mL of conc. HCl, 2 mL conc. HNO₃ and few drops of conc. H₂O₂. The solution is evaporated to dryness and the residue dissolved in 2 mL of conc. H₂SO₄, 1 mL conc. HNO₃ and about 100 mL redistilled water. After electrolysis of Cu, the solution is evaporated to 10 ml, transferred into a separatory funnel adding HCl in order to obtain a concentration of 8 mol L⁻¹. A 10-ml volume of isoamyl acetate is added and the obtained mixture is shaken for 5 min. After the phase separation the inorganic part is collected into a glass beaker, evaporated and the residue dissolved in 5 mL of 2 mol L⁻¹ HNO₃.

3. Results and Discussions

Previous investigations have shown very strong interference from matrix elements in trace elements determination by ETAAS [1, 9-15]. These facts pointed out to the necessity of trace elements separation from the matrix (copper and iron in the case of the investigated minerals) before the determination by ETAAS. After dissolution of the mineral samples, the method of the copper electrolysis using Pt-electrode is performed [16]. To check whether trace elements are electrolyzed together with copper, spiked samples with equal concentration of examined elements with and without copper are electrolyzed. It was not found that losses are recorded.

In the case of chalcopyrite, iron is present in the solution (after electrolysis) in high concentration. In this work we apply a method for separation of the chloride complex of iron by simple and rapid extraction into isoamyl acetate that effectively eliminates potential interference of iron [14]. To avoid interferences of chlorides and to concentrate the investigated elements, the inorganic layer is

evaporated and the residue dissolved in 5 mL of 2 mol L⁻¹ HNO₃.

The method is verified by the method of standard additions for the investigated elements and minerals. An exact amount of standard solutions with a known concentration of investigated elements is added to mineral sample. The result of investigated elements determination and the recovery are satisfactory and are given in Table 2.

Table 2. Determination of cadmium, cobalt, chromium, manganese, nickel and zinc in copper minerals by method of standard addition

Sample	<i>m</i> (add.)/ μg	<i>w</i> (calc.)/ μg g ⁻¹	<i>w</i> (find.)/ μg g ⁻¹	R (%)
Cd				
Brochantite			0.42	
	0.1	1.42	1.47	103.5
Chalcanthite			2.82	
	0.1	3.82	3.50	91.6
Chalcopyrite			54.9	
	5	102.1	105.2	103.0
Covellite			0.23	
	0.1	1.22	1.30	106.5
Native Cu			2.07	
	0.2	4.13	4.00	97.3
Co				
Brochantite			6.67	
Chalcanthite			2.82	
Chalcopyrite			19.5	
	2.0	39.5	33.24	84.2
Covellite			8.88	
	1.0	28.8	24.2	84.0
Native Cu			2.51	
	1.0	12.81	14.0	109.3
			24.3	105.1
	2.0	23.11		
Cr				
Brochantite			0.59	
	0.1	1.58	1.48	93.7
Chalcanthite			2.24	86.8
	0.2	2.58		
Chalcopyrite			1.63	
	0.1	2.63	2.52	95.8
Covellite			80.3	
	5.0	127.5	123.5	96.9
Native Cu			189.0	105.5
	10.0	179.0		
			0.10	
	0.2	2.0	1.94	97.0

Table 2 (continuation)

Sample	<i>m</i> (add.)/ μg	<i>w</i> (calc.)/ μg g ⁻¹	<i>w</i> (find.)/ μg g ⁻¹	R (%)
Native Cu			0.64	
	0.1	1.67	1.57	94.0
Mn				
Brochantite			10.47	
Chalcanthite			661.1	
	5.0	710.9	705.2	99.2
Chalcopyrite			184.7	
Covellite			5.97	
Native Cu			91.44	90.4
	10.0	104.1		
			3.98	
Ni				
Brochantite			34.56	
	0.5	39.52	42.86	108.4
Chalcanthite			62.02	
	5.0	85.80	84.06	98.0
Chalcopyrite			34.86	
	5.0	82.07	78.37	95.5
Covellite			2.14	
Native Cu			8.15	
Zn				
Brochantite			22.80	
	1.0	32.72	35.70	109.1
Chalcanthite			40.42	94.7
	2.0	42.70		
Chalcopyrite			167.1	
	10.0	258.0	268.4	104.0
Covellite			947.0	
Native Cu			6.25	
			20.8	

As it can be seen, the content of cadmium, cobalt and chromium trace elements is very low in the studied brochantite, chalcanthite, covellite and native copper. On the other hand, the similar situation is observed for the content of manganese, nickel and zinc in both latter minerals. Higher content of zinc and manganese in chalcopyrite is due to the possible contamination from sphalerite mineral (ZnS) being the dominant mineral in the Sasa mine. The concentration of iron is much higher compared to the other elements ranging from 98.3 μg g⁻¹ in native copper to 905.5 in covellite.

The determination of the investigated elements is also performed in the reference standard of copper concentrate (NR-3). It is found that, using the

proposed method; the determined content for cobalt and nickel is very close to the certified values.

A calibration curves are made using the proposed procedure for standard solutions of the investigated elements. The standard deviation (SD) of the blank sample ($n=5$) is: $0.001 \mu\text{g}\cdot\text{g}^{-1}$ for Cd, $0.005 \mu\text{g}\cdot\text{g}^{-1}$ for Cr, $0.1 \mu\text{g}\cdot\text{g}^{-1}$ for Co, Ni and Mn. Relative standard deviations range from 0.5 % to 2 %. Detection limits of the method, calculated as 3 SD of the blank, are $5 \text{ ng}\cdot\text{g}^{-1}$ for Cd, $15 \text{ ng}\cdot\text{g}^{-1}$ for Cr and $0.3 \mu\text{g}\cdot\text{g}^{-1}$ for Co, Ni and Mn, determined by Zeeman ETAAS, and $1.2 \mu\text{g}\cdot\text{g}^{-1}$ for Zn and $8.3 \mu\text{g}\cdot\text{g}^{-1}$ for Fe, determined by flame AAS. It is obvious that the levels are much higher when the determination is performed by flame AAS compared to ETAAS.

4. Conclusion

It is shown that cadmium, chromium, cobalt, iron, nickel, manganese, and zinc could be determined by both flame and electrothermal atomic absorption spectrometry in different copper minerals brochantite, chalcantite, chalcopyrite, covellite and native copper after electrolytic separation of copper and extraction separation of iron with isoamyl acetate from 8 mol l^{-1} HCl media for copper-iron minerals.

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6. References

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1. T. Stafilov, *Spectrochim. Acta, Part B*, **55**, 893 (2000).
2. V. B. Schweizer, *At. Absorpt. Newsl.*, **14**, 137 (1975).
3. P. Robinson, *Chem. Geol.*, **28**, 135 (1980).
4. T. Nakamura, K. Okubo, J. Sato, *Anal. Chim. Acta*, **209**, 287 (1988).
5. A. Lazaru, T. Stafilov, *Geologica Macedonica*, **7**, 73 (1993).
6. E. M. Donaldson, *Talanta*, **36**, 543 (1989).
7. M. Ure, R. Thomas, D. Littlejohn, *Int. J. Environ. Anal. Chem.*, **51**, 65 (1993).
8. G. Ilgen, J. J. Fiedler, *Chem. Erde*, **51**, 141 (1991).
9. T. Stafilov, A. Lazaru, E. Pernicka, *Acta Chim. Slo.*, **40**, 37 (1993).
10. T. Stafilov, S. Aleksovska, V. Jordanovska, *N. Jb. Miner. Abh.*, **167**, 401 (1994).
11. T. Stafilov, A. Lazaru, E. Pernicka, *At. Spectrosc.*, **16**, 158 (1995).
12. A. Lazaru, T. Stafilov, *Fresenius' J. Anal. Chem.*, **360**, 726 (1998).
13. D. Zendelovska, T. Stafilov, *Anal. Sci.*, **17**, 425 (2001).
14. T. Stafilov, D. Zendelovska, *Turkish J. Chem.*, **26**, 271 (2002).
15. A. Lazaru, T. Stafilov, *Bull. Chem. Technol. Macedonia*, **19**, 21-26 (2000).
16. D. Skoog, D. M. West, F. M. Holler, *Analytical Chemistry*, Školjska knjiga, Zagreb, 1999.