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DETERMINATION OF Co, Ni, Cr AND Cu IN GALENA AND SPHALERITE BY ZEEMAN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Abstract: Methods for the determination of Co, Ni, Cu and Cr in galena (PbS) and sphalerite (ZnS) by Zeeman electrothermal atomic absorption spectrometry have been proposed. Interferences were investigated by measuring the absorbance of Co, Ni, Cu and Cr in series of samples with varying mass ratios of investigated elements and potential interfering elements (Pb and Zn). Since, it was found that there is no interference in the determined mass ratios of the matrix and the investigated elements, Co, Ni, Cu and Cr were directly analyzed from the solution obtained by dissolution of galena in mineral acids (HCl and HNO_3). In the case of sphalerite Co, Ni and Cr were directly analyzed from the solution. Results show that the interfering element (Zn) tend to decrease the absorbance of copper at high concentrations. The procedure was verified by the method of standard additions and the results were compared with those obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Investigated minerals originate from different lead and zinc mines from the Republic of Macedonia.

It was found that the content of Co, Cr and Ni in galena ranges from 0.5 to 5 $\mu g \cdot g^{-1}$ and of Cu from 10 to 50 $\mu g \cdot g^{-1}$; and that the content of Cr in sphalerite ranges from 1 to 10 $\mu g \cdot g^{-1}$, of Ni from 10 to 50 $\mu g \cdot g^{-1}$ and of Co from 100 to 500 $\mu g \cdot g^{-1}$. It was also found that the detection limit (calculated as 3 standard deviations of the blank) for all investigated elements in both minerals is 0.05 $\mu g \cdot g^{-1}$.

Key words: determination; cobalt; chromium; nickel; copper; Zeeman electrothermal atomic absorption spectrometry; galena; sphalerite

INTRODUCTION

Minerals are naturally occurring inorganic substances having a relatively constant chemical composition. However, there is possibility of contamination, with the result that most minerals contain extraneous substances, and these often change the characteristics somewhat. In the other side detection of trace elements in the mineral sample helps to establish the condition in which these minerals had been formed, e.g., it helps to broaden the known geology of different mines. Galena (PbS) and sphalerite (ZnS) are minerals used for the production of lead and zinc. During the metallurgical processes it is possible to produce some other metals presence in the minerals as trace elements. Therefore, it is important to follow the content of some trace elements in these minerals.

Detection of trace elements in the mineral samples helps to establish the conditions in which these minerals had been formed, e.g., it helps to broaden the known geology of different mines. Therefore, it is important to follow the content of cobalt, copper, nickel and chromium in some sulfide minerals (galena and sphalerite) in lead and zinc mines from the Republic of Macedonia.

There are a number of investigations concerning the determination of elements investigated in similar geological samples by flame (FAAS) and electrothermal atomic absorption spectrometry (ETAAS). Some authors have investigated the possibility of the determination of these elements directly from the sample solution, by flame AAS (Beccaluva and Venturelli, 1971; Vasile and Collos, 1971; Rubeska and Miksovsky, 1974; Robert and Mallett, 1975; Srivastava, 1977; Alvin and Gardner, 1986; Zorkin and Zubova, 1990), or by ETAAS (Schmidt and Falk, 1987; Zheng and Su, 1993; Lazaru and Stafilov, 1993). The influence of interfering elements was of particular interest: in the flame AAS determination (Sundberg, 1973; Hannaker and Hughes, 1977; Wang, 1980), or in the ETAAS determination (Matsusaki et al., 1981; Subramanian, 1988). To overcome such interferences, the addition of different matrix modifiers or the separation and concentration methods were suggested (Hannaker and Hughes, 1977; Wang 1980; Subramanian, 1988; Donaldson, 1989; Isshiki et al., 1989; Li and Shu, 1992; Becerio-Gonzales, et al., 1993).

In this work we propose a method for directly determination of Co, Ni, Cr and Cu with Zeeman electrothermal atomic absorption spectrometry from the solution obtained by dissolution of minerals galena and sphalerite in mineral acids. Minerals galena and sphalerite originated from some lead and zinc mines from the Republic of Macedonia.

EXPERIMENTAL

Instrumentation

A SpectrAA 640 Z Zeeman atomic absorption spectrophotometer with a Varian PSD-100 Autosampler was used. Hollow cathode lamp was used as a source. Operating conditions for the determination of Co, Ni, Cr and Cu are given in Table 1.

Table 1

Instrumental parameters for determination of Co, Ni, Cu and Cr by ETAAS

Parameters	Co	Ni	Cu	Cr
Wavelength, nm	242.5	232.0	327.4	357.9
Slit, nm	0.2	0.2	0.5	0.5
Lamp current, mA	7.0	4.0	4.0	5.0
Calibration mode	Absorbance, peak height			
Background correction	Zeeman			
DRY				
Temperature, °C	120	120	120	120
Ramp time, s	45	45	45	45
Hold time, s	10	10	10	10
PYROLYSIS				
Temperature, °C	750	800	800	1000
Ramp time, s	5	5	5	5
Hold time, s	3	3	3	3
ATOMIZE				
Temperature, °C	2300	2400	2300	2600
Ramp time, s	1	1	1	1
Hold time, s	2	2	2	2
CLEAN				
Temperature, °C	2400	2500	2400	2600
Ramp time, s	1	1	1	1
Hold time, s	2	2	2	2
GAS	Argon			

Reagent and samples

All reagents and standards were of analytical grade. Stock solutions of Co, Ni, Cr and Cu were prepared by dissolving $CoCl_2 \cdot 6H_2O$, Ni, K_2CrO_4 and $CuCl_2 \cdot 6H_2O$. The mass concentration of solutions were 1000 mg/l, and from these solutions other diluted solutions were prepared.

Galena samples were collected in Zletovo and Sasa mines and sphalerite samples were collected in Toranica and Zletovo mines (Republic of Macedonia).

Procedure

1. *Sphalerite*

Mass of 0.1 to 0.5 g of powdered sample of sphalerite was dissolved in 15 cm^3 of 2 $mol \cdot dm^{-3}$ HNO_3. The solution was evaporated to dryness and the residue was dissolved in 5 ml of 2 $mol \cdot dm^{-3}$ HNO_3 with a minimum of boiling. The solution was filtered and transferred to a volumetric flask of 100 cm^3.

2. *Galena*

Mass of 0.1 to 0.5 g of powdered sample of galena was dissolved in 10 cm^3 of concentrated HNO_3 and 2 cm^3 of H_2O_2. The solution was evaporated to dryness, the residue was dissolved in 2 cm^3 of concentrated HNO_3 and 10 cm^3 of 2 $mol \cdot dm^{-3}$ HNO_3 and the solution was filtrated and transferred into a volumetric flask of 100 cm^3.

RESULTS AND DISCUSSION

In most papers on the determination of Co, Ni, Cr and Cu in different geological samples acid digestion is suggested for samples dissolution. However, these solutions contain different ions, which may interfere in the determination of Co, Ni, Cr and Cu by Zeeman ETAAS. Therefore, the first step in this work was to investigate the matrix interferences. For this purpose, series of solutions with constant mass of Co, Ni, Cr, and Cu and varying masses of potential interfering elements (Pb and Zn) were prepared and interferences were investigated by measuring the absorbance of Co, Ni, Cr and Cu from solutions. Results of interference investigation of zinc and lead on the absorbance of Co, Ni, Cr and Cu are given in Fig. 1 and Fig. 2.

It can be seen from the Figs. 1 and 2, that Ni and Co can be determinated from sphalerite and galena in the cases when the mass ratio is less than $50 \cdot 10^4$, corresponding to 0.58 g of mineral mass. In galena directly determination of Cu is possible when 0.1 g of mass is used (Fig. 1). Zinc interferes on the determination of Cu by decreasing the Cu absorbance (Fig. 2) when the mass rations for Cu and Zn is higher than 1:1000 and directly determination of Cu in sphalerite is not possible. Lead and zinc also interfere on the determination of Cr by increasing the Cr absorbance, when the mass rations for Cr and Pb is higher than 1:1000000, for Cr and Zn is higher than 1:400000. The investigations show that Cr can be directly determinated when 0.28 g of galena and 0.15 g of sphalerite are used.

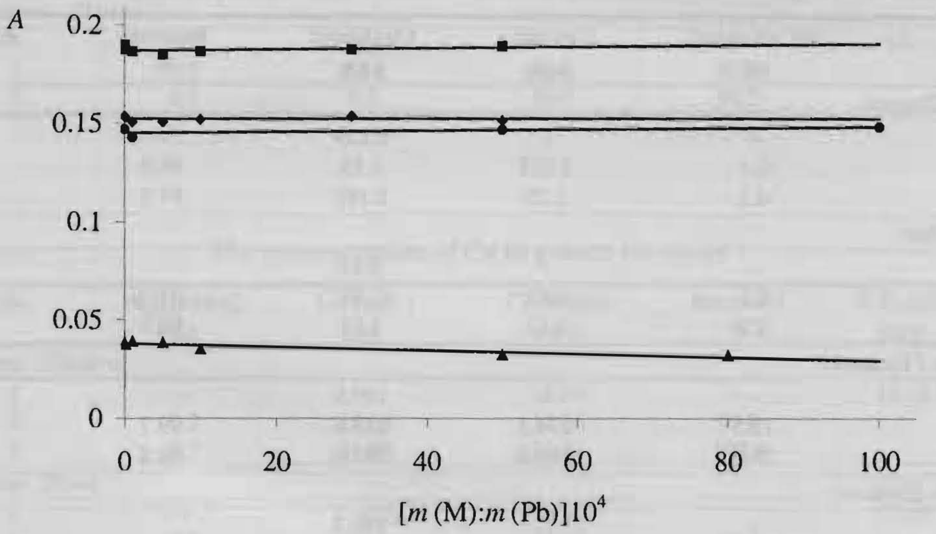

Fig. 1. Interference of lead on the absorbance of Co (■), Ni (◆), Cr (●) and Cu (▲)

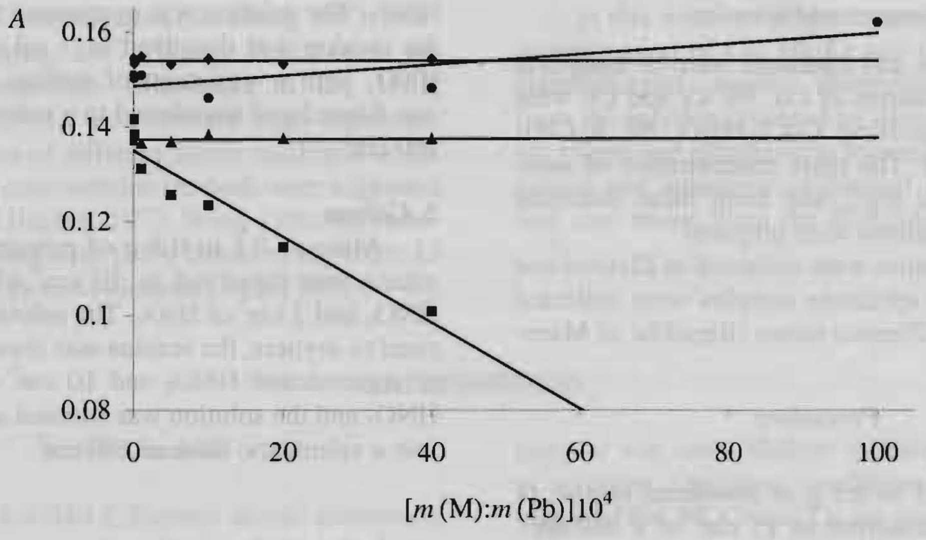

Fig. 2. Interference of zinc on the absorbance of Ni (▲), Co (◆), Cr (●) and Cu (■)

The method was verified by the method of standard additions for the investigated elements and minerals. The value of the recovery ranges from 95 to 101.8 % (Tables 2–5). These results were compared with those obtained by inductively coupled plasma-atomic emission spectrometry (ISP-AES). It was found that the obtained data from both techniques are similar.

Using this method some samples of galena and sphalerite from Sasa, Zletovo and Toranica mines from the Republic of Macedonia (with and without standard additions) cobalt, nickel, copper and chromium were determined. It was found that the content of Co, Cr and Ni in galena ranges from 0.5 to 5 $\mu g g^{-1}$ and of Cu from 10 to 50 $\mu g g^{-1}$; and that the content of Cr in sphalerite ranges from 1 to 10 $\mu g g^{-1}$, of Ni from 10 to 50 $\mu g g^{-1}$ and Co from 100 to 500 $\mu g g^{-1}$.

It was also found that the detection limit, calculated as 3 standard deviations (*s*) of the blank, for all investigated elements in both minerals is 0.05 $\mu g g^{-1}$. The obtained values for the content of some of the investigated elements in galena and sphalerite are in good agreement with those of Serafimovski et al., 1997.

Table 2

The concentration of Co in galena and sphalerite (in μg/g)

Sample	m(Co)(added) μg	Co (calc.) μg/g	Co (found) μg/g	Recovery %	ICP-AES μg/g
Galena (Zletovo)					
1	–	–	0.259	–	<2.5
2	0.1	1.257	1.19	95.0	
3	0.2	2.25	2.193	97.5	
Galena (Sasa)					
1	–	–	0.63		<2.5
2	0.1	1.63	1.64	100.6	
3	0.2	2.62	2.58	98.5	
Sphalerite (Toranica)					
1	–	–	149.9		–
2	12.5	274.3	273.6	99.7	
3	25.0	398.4	397.6	99.8	
Sphalerite (Zletovo)					
1	–	–	393.3		–
2	25.0	642.1	651.74	101.5	
3	50.0	890.3	884.69	99.4	

Table 3

The concentration of Ni in galena and sphalerite (in μg/g)

Sample	m_{Ni} (added) μg	Ni (calc.) μg/g	Ni (found) μg/g	R %	ICP-AES μg/g
Galena (Zletovo)					
1	–	–	2.62	–	2.32
2	200.0	4.62	4.42	95.7	
3	500.0	7.61	7.52	98.8	
Galena (Sasa)					
1	–	–	1.43	–	1.80
2	200.0	3.42	3.36	98.2	
3	500.0	6.4	6.34	99.1	
Sphalerite (Toranica)					
1	–	–	25.57	–	25.70
2	200.0	27.57	28.24	102.4	
3	500.0	30.55	30.98	101.4	
Sphalerite (Zletovo)					
1	–	–	13.5	–	12.95
2	200.0	15.5	15.5	100.0	
3	500.0	18.49	18.5	100.1	

Table 4

The concentration of Cr in galena and sphalerite (in μg/g)

Sample	m_{Cr} (added) μg	Cr (calc.) μg/g	Cr (found) μg/g	Recovery %	ICP-AES μg/g
Galena (Zletovo)					
1	–	–	0.82	–	<5
2	0.1	1.82	1.77	97.3	
3	0.2	2.81	2.8	99.6	
Galena (Sasa)					
1	–	–	0.97	-	<5
2	0.1	1.97	1.97	100.0	
3	0.2	2.96	2.95	99.7	
Sphalerite (Toranica)					
1	–	–	4.87	–	<5
2	0.1	5.86	5.84	99.7	
3	0.2	6.86	6.98	101.7	
Sphalerite (Zletovo)					
1	–	–	4.51	–	<5
2	0.2	6.51	6.41	98.5	
3	0.5	9.5	9.43	99.3	

Table 5

The concentration of Cu in galena (in μg/g)

Sample	m_{Cu} (added) μg	Cu (calc.) μg	Cu (found) μg/g	Recovery %	ICP-AES μg/g
Galena (Zletovo)					
1	–	–	16.04	–	14.16
2	0.2	18.04	17.86	99.0	
3	0.5	21.03	21.54	102.4	
Galena (Sasa)					
1	–	–	29.60		27.45
2	0.2	31.8	31.67	99.6	
3	0.5	34.79	34.7	99.7	

CONCLUSION

Cobalt, nickel, chromium and copper can be determinated by Zeeman electrothermal atomic absorption spectrometry in galena and sphalerite. There is no interference in the determined mass ratios of the matrix and the investigated elements (Co, Ni, Cu and Cr) can be analyzed directly from the solution obtained by dissolution of galena and sphalerite in mineral acids (HCl and HNO_3), except in the case of the determination of copper in sphalerite when the interfering element (Zn) tend to decrease the absorbance of copper at high concentrations. The procedure was verified by the method of standard additions and the results were compared with those obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

It was found that the content of Co, Cr and Ni in galena ranges from 0.5 to 5 μg/g and of Cu from 10 to 50 μg/g; and that the content of Cr in sphalerite ranges from 1 to 10 μg/g, of Ni from 10 to 50 μg/g and of Co from 100 to 500 μg/g. It was also found that the detection limit (calculated as 3 standard deviations of the blank) for all investigated elements in both minerals is 0.05 μg/g.

REFERENCES

Alvin J. F., Gardner F. R., 1986: *Determination of Cu, Fe, Pb and Zn in complex sulfide materials by flame atomic absorption spectrometry.* Analyst, 111, 897–9.

Beccaluva L., Venturelli G., 1971: *Nickel, chromium and strontium determination in some silicate rock.* At. Absorpt. Newslett., 10, 50–52.

Becerio-Gonzales E., Bemejo-Barrera P., Bermejo-Barrera A., Barciela-Garcia J., Barciela-Alonso C., 1993: *Speciation of chromium by the determination of total chromium and chromium(III) by electrothermal atomic absorption spectrometry.* J. Anal. At. Spectrom., 8, 649–53.

Donaldson E. M., 1989: *Determination of cobalt, nickel, lead, bismuth, and indium in ores, soils, and related materials by atomic absorption spectrometry after separation by xanthate extraction.* Talanta, 36, 543–548.

Hannaker P., Hughes T. C., 1977: *Multielement trace analysis of geological materials with solvent extraction and flame atomic absorption spectrometry.* Anal. Chem., 49, 1485–8.

Isshiki K., Sohrin Y., Karatani H., Nakayama E., 1989: *Preconcentration of chromium(III) and chromium(VI) in seawater by complexation with quinolin-8-ol and adsorption on macroporous resin.* Anal. Chim. Acta, 224, 55–64.

Lazaru A., Stafilov T., 1993: *Determination of Fe, Mn, Cu, Cr and Ni in sulfide minerals from Alšar by atomic absorption spectrometry.* Geologica Macedonica, 7, 73–80.

Li S., Shu Z., 1992: *Atomic absorption spectroscopy determination of traces of nickel in geological samples after separation by solvent flotation.* Lihua Jianyuan Huaxue fence, 28, 350–352; CA, 119, 261630q (1993).

Matsusaki K., Yoshino T., Yamamoto Y., 1981: *Removal of chloride interferences in the determination of chromium by atomic absorption spectrometry with electrothermal atomization.* Anal. Chim. Acta, 124, 163–8.

Robert R. V. D., Mallett R. C., 1975: *Determination by atomic absorption spectrometry of minor elements in zinc, lead and copper sulfide concentrate.* Natl. Inst. Metall., Rep. S. Afr., Rep., 1975: 1746–1749.

Rubeska I., Miksovsky M., 1974: *Analysis of sulfatidic minerals by atomic absorption spectrometry.* Czech. Chem. Commun., 39, 3485–93.

Schmidt K. P., Falk H., 1987: *Direct determination of silver, copper and nickel in solid materials by graphite furnace atomic absorption spectrometry using a specially designed graphite tube.* Spectrochim. Acta, 42B, 431–43.

Serafimovski T., Spasovski O., Stankovski R., 1997: *Content and distribution of some elements in the major minerals from the Toranica Pb-Zn deposit (NE Macedonia).* Geologica Macedonica, 11, 1–15.

Srivastava R. K., 1977: *A comprehensive atomic absorption and spectrophotometric sheme for the determination of major and trace elements in rocks and minerals.* Neues Jarhb. Mineral., Monatsh., 9, 425–432.

Subramanian K. S., 1988: *Determination of chromium(III) and chromium(VI) by ammonium pyrolidinecarbamate-methylisobuthyl ketone – furnace atomic absorption spectrometry.* Anal. Chem., 60, 11–15.

Sundberg L. L., 1973: *Interferences in Ni determinations by AAS.* Anal. Chem., 45, 1460–4.

Zorkin I. D., Zubova O. D., 1990: *Determination of lithium, rubidium, cesium, strontium, copper, zinc, lead, cobalt, nickel, and chromium in silicate rock by atomic spectroscopy.* Zh. Anal. Khim., 45, 1858–1860.

Vasile I., Collos E., 1971: *Determination of cobalt and nickel in sulfide minerals by atomic absorption spectrophotometry.* Lucr. Conf. Nat. Chim. Anal., 2, 99–104.

Zheng Y., Su X., 1993: *Application of standardless analysis in graphite furnace atomic absorption spectrometry: determination of chromium.* Talanta, 40, 347–50.

Wang W.-I., 1980: *Determination of trace chromium(VI) as a thiosemicarbazide complex by solvent extraction and atomic absorption spectrometry.* Anal. Chim. Acta, 119, 157–60.

Резиме

ОПРЕДЕЛУВАЊЕ НА Co, Ni, Cr И Cu ВО ГАЛЕНИТ И СФАЛЕРИТ СО ZEEMAN-ОВА ЕЛЕКТРОТЕРМИЧКА АТОМСКА АПСОРПЦИОНА СПЕКТРОМЕТРИЈА

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Клучни зборови: определување; кобалт; хром; никел; бакар; Zeeman-ова електротермичка атомска апсорпциона спектрометрија; сфалерит; галенит

Предложен е метод за определување на Co, Ni, Cu и Cr во галенит и сфалерит со Zeeman-ова електротермичка атомска апсорпциона спектрометрија. Извршено е испитување на влијанието врз апсорбанцата на Co, Ni, Cr и Cu во серии од проби со променливи масени односи на испитуваните елементи и потенцијалните интерферентни елементи (Pb и Zn). Испитувањата покажаа дека при утврдени масени односи нема влијание и затоа е можно директно определување на Co, Ni, Cu и Cr од растворите добиени со растворањето на галенитот и сфалеритот со минерални киселини (HCl и HNO_3), освен во случајот на определувањето на Cu во сфалерит. Резултатите покажуваат дека интерферентиот елемент (Zn) ја намалува апсорбанцата на Cu кога е присутен во високи концентрации. Постапката е проверена со методот на стандардни додатоци и со споредба на резултатите со оние добиени со атомска емисиона спектрометрија со индуктивно спрегната плазма (ICP-AES). Испитуваните минерали потекнуваат од различни рудници за олово и цинк од Република Македонија.

Најдено е дека содржината на Co, Cr и Ni во галенит се движи од 0,5 до 5 μg/g, а на бакарот од 10 до 50 μg/g, додека содржината на хром во сфалерит се движи од 1 до 10 μg/g, на Ni од 10 до 50 μg/g и на Co од 100 до 500 μg/g. Границата на детекција за испитуваните елементи во двата минерала изнесува 0,05 μg/g.