NT — 2

DETERMINATION OF COBALT AND ZINC IN SOME MINERALS FROM ALSHAR MINE BY ATOMIC ABSORPTION SPECTROMETRY

Anna Lazaru and Trajče Stafilov

Institute of Chemistry, Faculty of Science, St. Kiril and Metodij University. POB 162, 91001 Skopje, Republic of Macedonia

ABSTRACT: In this paper, the methods for determination and the results of cobalt and zinc in thallium-arsenic (lorandite), arsenic (realgar and orpiment), antimony (stibnite) and iron (marcasite) sulfide minerals and dolomite as well as, by atomic absorption spectrometry, are presented. The investigation of the interferences showed that it is possible to determine these elements directly from the obtained solutions. Cobalt was determined by electrothermal and zinc by flame atomic absorption spectrometry. Using these methods, cobalt and zinc were determined in different mineral samples taken from Alshar deposit, Macedonia.

INTRODUCTION

The LOREX project, is based on the idea that the mineral lorandite ($TlAsS_2$) from Alshar deposit (Macedonia) could be used as a solar neutrino detector (1). The aim of this project is to determine the content of ^{205} Pb accumulated in the thallium minerals from Alshar, especially in lorandite ($TlAsS_2$), which is produced in the nuclear reaction between solar neutrinos and ^{205} Tl.

Therefore, it is necessary to determine exactly the lead content in the thallium or other minerals(2-4) and the content of thallium in nonthallium minerals (5), but it is also necessary to determine the content of the other elements in these minerals present in Alshar deposit, such as: realgar (As_4S_4), orpiment (As_2S_3), stibnite (Sb_2S_3), marcasite (FeS_2) and dolomite ($CaMg(CO_3)_2$).

For the application of this experiment it is very important to determine the content of the other elements, as: Fe, Mn, Cu, Cr, Ni, Co, Zn, Bi, U, Th, Hg etc., especially those which are involved in background reactions which produce Pb. Also, detection of these elements and their concentrations in the ore and mineral samples helps to establish the conditions in which these elements have been formed, e.g., it helps to spread the knowledge of the geology of the Alshar mine.

Until now, there are very little literature values about the content of cobalt and zinc in these minerals. There are few results given by Palme et al. (2) obtained by neutron activated analysis and by Boev et al. (6) Abtained by mass spectrometry.

There are a number of investigations concerning the determination of Co and Zn in similar geological samples by atomic absorption spectrometry (AAS). Some authors have investigated the possibility to determine of these elements directly from the sample solutions, by flame AAS (for cobalt (7, 8) and for zinc (8, 10) or by electrothermal AAS — ETAAS (for cobalt (11-13) or for zinc (14, 15). However, in the most cases, the influence of interfering elements was of particular interest in the ETAAS determination (12, 16). To overcome such interferences, it was suggested on addition of different matrix

modifiers in ETAAS determination (13), or separation and concentration of these elements from the matrix and their determination by AAS (16-19).

In this work we propose a method for the Co and Zn determination by atomic absorption spectrometry. It was suggested that it is possible to determine these elements directly from the obtained solution of the investigated minerals.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer 703 and 303 atomic absorption spectrophotometers, an HGA-400 and HGA-72 and M56 recorder, were used. A hollow cathode lamps were used as a source. Operation conditions for the determination of Co and Zn are given in Table 1.

Table I. Instrumental parameters for determination of Co (by ETAAS) and Zn (by flame AAS)

Parameter	Cobalt	Zinc
Wavelength	279.5 nm	213.9 nm
Slit	0.2 nm	0.7 nm
Lamp current	20 mA	20mA
Calibration mode	Absorbance, peak height	Absorbance, peak Height
Gas mixture		Acetylene-Air

Graphite furnace for Co			
	Temperature, °C	Time, s	Ramp time, s
DRY	110	30	2
CHAR	700	30	1
ATOMIZE	2400	5	0
CLEAN	2700	3	1
GAS		Argon	

Procedures

Realgar and orpiment. 0.1 to 1.0 g of powdered samples of realgar or orpiment were dissolved in 5 cm^3 concentrated HNO$_3$. The solution was evaporated to dryness, and then the residue was dissolved in 10 cm^3 of concentrated HCl and a few drops of H$_2$O$_2$ with a minimum boiling. Then, the solution was transferred to a volumetric flask of 25 (or 50) cm^3. From this solution a volume of 20 mm^3 was introduced to a graphite furnace.

Stibnite and dolomite. 0.1 to 1.0 g of powdered mineral samples were dissolved in 5 cm^3 concentrated HCl, 1 cm^3 concentrated HNO$_3$ and a few drops of H$_2$O$_2$. The solution was evaporated to dryness, and then the residue was taken up in 10 cm^3 of concentrated HCl.

Marcasite. 0.1 to 1.0 g of powdered mineral samples were dissolved in 5 cm^3 concentrated HCl, 5 cm^3 concentrated HNO$_3$ and a few drops of H$_2$O$_2$. The solution was evaporated to dryness, and then the residue was taken up in 10 cm^3 of concentrated HCl.

Lorandite. 0.1 to 1.0 g of powdered mineral samples were dissolved in 15 cm^3 concentrated HCl, 3 cm^3 concentrated HNO$_3$ and a few drops of H$_2$O$_2$. The solution was evaporated to dryness, and then the residue was taken up in 15 cm^3 of concentrated HCl.

RESULTS AND DISCUSSION

In most papers on the determination of investigated elements by ETAAS in different geological samples, acid digestion is suggested for sample dissolution. However, these solutions contain different ions of elements dissolved from the sample matrix, which may interfere with the determinations. Therefore, it is necessary to investigate this eventually present interfering.

Table III. Determination of Co and Zn by method of standard additions

Mineral	w (added)	w (calculated)	w (found)	R (%)
		COBALT		
Realgar				
1	—	—	0.0	—
2	19.92	19.92	18.92	95.0
3	39.92	39.92	39.92	100.0
Orpiment				
1	—	—	0.0	—
2	10.02	10.02	10.02	100.0
3	20.00	20.00	20.00	100.0
Marcasite				
1	—	—	21.9	—
2	10.04	31.94	32.43	101.5
3	20.000	41.90	42.00	100.2
Dolomite				
1	—	—	10.73	—
2	4.99	15.72	15.97	101.6
3	9.90	20.63	19.80	95.5
		ZINC		
Realgar				
1	—	—	67.17	—
2	40.88	108.0	97.9	90.6
3	61.44	128.6	130.7	101.7
Orpiment				
1	—	—	28.02	—
2	41.02	69.04	68.47	99.2
3	61.43	89.45	92.81	103.8
Marçasite				
1	—	—	66.92	—
2	41.14	108.1	110.8	102.5
Dolomite				
1	—	—	25.95	—
2	20.48	46.43	46.11	99.3

The interferences of matrix elements of the minerals studied (As, Sb, Tl, Fe, Ca and Mg) on the determination of Co and Zn, were investigated by preparing of series of solutions with the same concentration of investigated elements and different concentrations of interfering similar to the concentrations in the sample solutions. The results of this interferences in the determination of Co by ETAAS show that there are very little interference from As, Sb, Tl, Fe Ca and Mg on the determination of Co when the mass concentration of As, Sb and Tl is not higher than 12.5 mg cm^{-3}, and of Fe, Ca and Mg up to 1.25 mg.cm^{-3}. From the obtained results it can be seen that Co can be determined from realgar, orpiment, stibnite and lorandite when 1 g of mass is used, and in the case of marcasite and dolomite not more than 250 mg in 50 cm^{-3}. In the case of the determination of Zn by flame AAS, similar results of the interferences were obtained.

The methods were checked by method of standard additions (Table III) and by determination of Co and Zn by these procedures in referent standard samples (Table IV). The obtained recovery values (R) in the method of standard addition are satisfactory (in range of 95.0 103.8%) and the obtained results for referent standard samples are very similar to certified values.

Table IV. Determination of Co and Zn in some referent standard samples (in%)

Referent sample	Cobalt w (certified)	w (found)	Zinc w (certified)	w (found)
Cu concentrate	0.074	0.073	—	0.051
SU-1	0.063	0.065	0.029	0.027
SU-1a	0.041	0.042	—	0.013
UM-1	0.035	0.036	0.01	0.008

Table V. The results of determination of Fe, Mn, Cr, Cu and Ni in the investigated minerals

Mineral	w/μg.g^{-1} Co	Zn	Mineral	w/μmg.g^{-1} Co	Zn
Lorandite			P-21-2	38.0	88.0
pure	40.3	141.0	P-21-3	10.0	28.0
impure	103.0	239.9	P-21-4	4.0	5.6
Orpiment			R-1	2.5	29.0
h-800-1	< 1·0	9-4	Stibnite		
h-800-2	< 1.0	< 1.0	S-1	13.7	50.0
h-800-3	< 1.0	52.0	Dolomite		
h-800-4	4.0	34.4	h-800-1	64.4	48.0
A-1	2.0	18.8	h-800-2	59.4	< 1.0
Realgar			h-800-3	59.8	15.4
h-800-1	< 1.0	27.9	D-1	64.5	—
h-800-2	< 1.0	17.8	Marcasite		
h-800-3	< 1.0	18.9	M-1	5.0	87.5
from orpim.	< 1.0	< 1.0	from realgar		
P-21-1	24.0	56.0	P-21	120.0	1088.0

Using these methods, Co and Zn were determined in different samples of investigated minerals. Obtained results are given in Table V. As it can be seen, content of Co in realgar and orpiment is usually low (below 1 μg · g^{-1}), except in a few cases where the concentration is from 10-30 μg · g^{-1}. In one sample of lorandite it was found 40.3 mg · g-1, of stibnite 13.7 μg · g^{-1}, and of marcasite 5 μg · g^{-1}. But in impure samples the contant of Co is higher (103 in lorandite, ar 120 μg · g^{-1} in marcasite). In four samples of dolomite the content of Co is very similar: from 59.4 to 64.5 μg · g^{-1}.

The content of Zn in the investigated minerals is higher than Co. Thus, the content of Zn in a few samples in realgar, orpiment, marcasite and dolomite is from 1-4, but in the other is up to 50 μg · g^{-1}. In one sample of lorandite it was found 141 μg · g^{-1}, and of marcasite 85.5 μg · g^{-1}. But, in impure samples the content of Zn is higher (239.9 in lorandite or 1088 μg · g^{-1}. In one sample of lorandite it was found 141 μg · g^{-1}, and of marcasite 85.5 μg · g^{-1}. But, in impure samples the content of Zn is higher (239.9 in lorandite or 1088 μg · g^{-1} in marcasite).

CONCLUSION

Co and Zn can be determined by atomic absorption spectrometry in some minerals (realgar, orpimnet, lorandite, stubnite, marcasite, dolomite) from Alshar mine, Macedonia. Zn can be analyzed by flame, and Co by electrothermal atomic absorption spectrometry. The content of these elements in the investigated minerals vary from below i for Co to 1000 μg · g^{-1} for Zn.

REFERENCES

1. M. S. Freedman, C. M. Stevens, E. P. Honwitz, L. H. Fuchs, J. Sherner, L. S. Goodman, W. J. Childs, Science, 193, 1117 (1976).
2. H. Palme, M. K. Pavicevic, B. Spetel, Nucl, Inst. Meth. Phys. Res. A271, 314 (1988).
3. T. Stafilov, V. Jordanovska, S. Aleksovska, Bull. Chem. Technol. Macedonia, 9, 159 (1990).
4. T. Stafilov. V. Jordanovska, S. Aleksovska, Vest, SLov. Kem. Drust., 37, 141 (1990).
5. T. Stafilov, A. Lazaru, E. Pernicka, Acta Chim. Slo., 40, 37 (1993).
6. B. Boev, T. Serafimovski, B. Milosavljević, Geologica Macedonica, 7, 41 (1993).
7. J. R. Castillo, J. M. Mir, M. C. Martinez, T. Gomez, At. Spectrosc., 9, 9 (1988).
8. J. S. Baros, Analyst (London), 114, 369 (1989).
9. M. D. K. Abo-Rady, Fresenius Z. Anal. Chem., 296, 380 (1979).
10. J. F. Alvin, F. R. Gardner, Analyst, 111, 897 (1986).
11. I. D. Zorkin, O. D. Zubova, Zh. Anal. Khim., 45, 1858 (1990).
12. R. Kuroda, T. Nakano, Y. Miura, K. Oguma, J. Anal. At. Spectrom., 1, 429 (1986).
13. T. Nakamura. H. Oka, S. Hidehiro, J. Sato, Analyst (London), 117, 131 (1992).
14. F. Shaw, J. M. Ottaway, Analyst (London), 100, 217 (1975).
15. F. J. Langmyhr, J. R. Strubergh, Y. Thomassen, J. E. Hanssen, J. Dolezal, Anal. Chim. Acta, 71, 35 (1974).
16. L. Ebdon, A. T. Ellis, R. W. Ward, Talanta, 29, 297 (1982).
17. E. M. Donaldson, Talanta, 36, 543 (1989).
18. J. R. Clark, J. G. Viets, Anal. Chem., 53, 65 (1981).
19. J. G. Viets, R. M. OLeary, J. R. Clark, Analyst (London), 109, 1589 (1984).