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DETERMINATION OF Zn, Mn AND Fe IN SOME MINERALS BY ATOMIC ABSORPTION SPECTROMETRY

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A b s t r a c t : A rapid and simple method for the determination of iron, manganese and zinc in some sulfide (galena and sphalerite), carbonate (siderite, aragonite) and sulfate (gypsum) minerals is based on atomic absorption spectrometry. The samples were dissolved in mixture of HNO_3 and HCl. The effects of interfering elements (Pb, Zn, Ca and Fe) on the determination of Fe, Mn and Zn in the investigated minerals were studied. These investigations show that it is possible to determine iron, manganese and zinc directly from solutions obtained by dissolution of minerals in mineral acids (HCl and HNO_3), except in the case of determination of manganese in calcium matrices. It was found that the presence of calcium tends to decrease the absorbance of manganese. Procedures were verified by the method of standard additions and results were compared with those obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES). It was also found that the detection limit for all investigated elements in minerals is 2 $\mu g \cdot g^{-1}$ for Zn and 5 $\mu g \cdot g^{-1}$ for Mn and Fe. Investigated minerals originate from different mines from the Republic of Macedonia.

Key words: iron; manganese; zinc; atomic absorption spectrometry; sphalerite; galena; siderite; aragonite; gypsum

INTRODUCTION

The principal advantage of flameless atomic absorption spectrometry, i.e. the detection limits, which are extremely low in comparison with other methods and are attainable for a great number of elements, makes this technique particularly suitable for determination of elements present in geochemical materials in concentration of the order of ppb. Iron, manganese and zinc are of great interest in geochemistry for better understanding and interpretation of various geological processes. There are a number of investigations concerning the determination of elements investigated in similar geological samples by flame atomic absorption spectrometry (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 (Rubeška and Miksovsky, 1974; Srivastava, 1977; Bichova and Kherebenko, 1978; Hannaker and Hou, 1984; Alvin and Gardner, 1986; Zorkin and Zubova, 1990; Lazaru and Stafilov, 1993), or by ETAAS (Lazaru and Stafilov, 1993). The influence of interfering elements was of particular interest: in the flame AAS determination (Hannaker and Hughes, 1977; Robinson, 1980; Marabini et al., 1982), or in the ETAAS determination (Tominaga and Umezaki, 1983).

In this work we propose a method for directly determination of Zn, Mn and Fe with atomic absorption spectrometry from the solution obtained by dissolution of investigated minerals in mineral acids.

EXPERIMENTAL

Instrumentation

Perkin-Elmer 303 atomic absorption spectrophotometer was used. Light sources were iron, manganese and zinc hollow cathode lamps. The instrumental parameters for the determination of Fe, Mn and Zn are given in Table 1.

Table 1

Instrumental parameters for determination of Zn, Mn and Fe by flame AAS

Parameters	Zn	Mn	Fe
Wavelength, nm	213.9	279.5	248.3
Slit, nm	1	0.2	0.2
Lamp current, mA	15	10	20
Gas mixture		Acetylene/air	

Procedures

Sphalerite. 0.1 to 0.5 g of powdered sample of sphalerite was dissolved in 15 ml of 2 mol/l HNO_3. The solution was evaporated to dryness and the residue was dissolved in 5 ml of 2 mol/l HNO3. The solution was transferred to a volumetric flask of 50 ml.

Galena. 0.1 to 0.5 g of powdered sample of galena was dissolved in 10 ml conc. HNO_3 and 2 ml of H_2O_2. The solution was evaporated to dryness, the residue was dissolved in 2 ml HNO_3 and 10 ml of 2 mol/l HNO_3 and the solution was transferred into a volumetric flask of 50 ml.

Siderite, aragonite, gypsum. 0.1 to 0.5 g of powdered mineral sample was dissolved in 5 ml of conc. HCl and 1 ml of conc. HNO_3. A few drops of H_2O_2 were added and the solution evaporated to near dryness. The residue was dissolved in 2 ml of concentrated HCl and the solution was transferred into a volumetric flask of 50 ml.

RESULTS AND DISCUSSION

Because it is sensitive and specific, atomic absorption spectrometry (AAS) is widely used in geochemical analysis. For sample dissolution usually an acid digestion is used. However, acid digestion produces solutions that contain different ions of elements dissolved from the sample matrix, which may interfere with the determination of iron, manganese and zinc. The interference of Pb, Zn, Ca and Fe as matrix elements was studied. Series of solutions with the same concentration of Fe, Mn and Zn and various concentrations of interfering elements were prepared, so that the concentrations of these elements were similar to the concentrations in the sample solutions. Results from these investigations are given on Figs. 1–4. As it can be seen, Fe, Mn and Zn can be determine in galena (Fig. 1), Fe in Ca-minerals (Fig. 2), Fe and Mn in sphalerite (Fig. 3) and Zn in siderite (Fig. 4) when 0.5 g of mass is used. Zn in Ca-minerals (Fig. 2) and in siderite (Fig. 4) can be directly determined when 0.25 g is used.

Using proposed methods, some samples of the investigated minerals (with and without standard additions) were dissolved and Fe, Mn and Zn were determinated. Results are given on Tables 2–4 and show satisfactory recovery values. These results are compared with those obtained by ICP-AES and similar results were obtained.

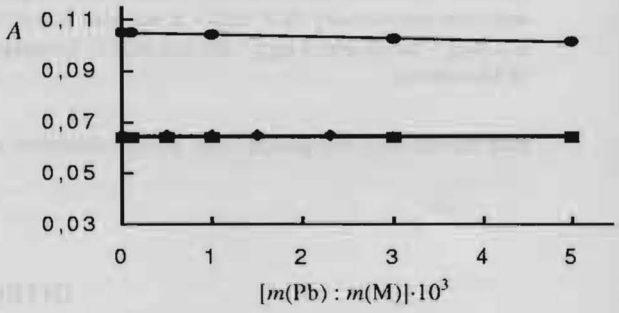

Fig. 1. Influence of Pb as matrix element on Fe (♦), Mn (■) and Zn (●) absorbance

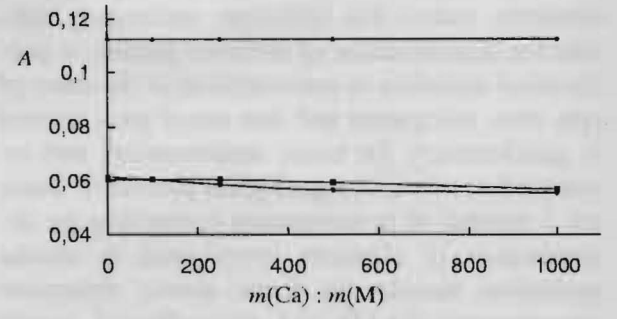

Fig. 2. Influence of Ca as matrix element on Fe (■), Zn (♦) and Mn (●) absorbance

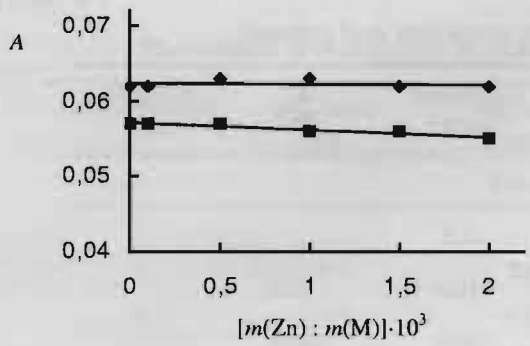

Fig. 3. Influence of Zn as matrix element on Fe (♦) and Mn (■) absorbance

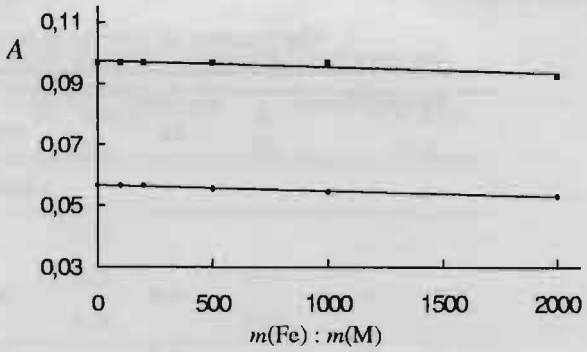

Fig. 4. Influence of Fe as matrix element on Mn (♦) and Zn (■) absorbance

Table 2

The content of iron in galena, sphalerite, aragonite and gypsum

Sample/Mineral	m_{Fe} (added) µg	w_{Fe} (calc.) µg/g	w_{Fe} (found) µg/g	*R* %	ICP-AES µg/g
		Galena – Zletovo			
1	–	–	77.15	–	80.60
2	10.0	176.85	179.5	101.5	
3	25.0	326.4	329.01	100.8	
		Galena – Sasa			
1	–	–	290.5	–	278.4
2	25.0	540.5	530.5	98.1	
3	50.0	790.0	794.71	100.6	
		Sphalerite – Zletovo			
1	–	–	4680.0	–	–
2	2000.0	6678.0	6743.0	100.9	
3	4000.0	8672.0	8762.0	101.03	
		Sphalerite – Toranica			
1	–	–	4484.0	–	–
2	2000.0	6482.0	6753.0	104.1	
3	4000.0	8476.0	8403.0	99.1	
		Aragonite			
1	–	–	305.0	–	–
2	10.0	404.6	406.4	100.4	
3	25.0	553.8	532.3	96.1	
		Gypsum – Delčevo			
1	–	–	266.0	–	309.6
2	25.0	516.0	515.0	99.8	
3	50.0	765.5	754.2	98.5	
		Gypsum – Probištip			
1	–	–	89.9	–	87.25
2	10.0	189.7	190.6	100.4	
3	25.0	338.2	323.7	95.7	

Table 3

The content of zinc in galena, siderite, aragonite and gypsum

Sample/Mineral	m_{Zn} (add.) μg	w_{Zn} (calc.) μg/g	w_{Zn} (found) μg/g	R %	ICP-AES μg/g
Galena – Sasa					
1	–	–	<2.0	–	–
2	10.0	100	110.0	110.0	
3	25.0	250	250.0	100.0	
Galena – Zletovo					
1	–	–	109.0	–	114.0
2	25.0	358.0	355.0	99.2	
3	50.0	608.0	592.0	97.4	
Siderite					
1	–	–	1280.0	–	–
2	50.0	1800	1890.0	105.0	
3	100.0	2280	2350.0	103.1	
Aragonite					
1	–	–	<2.0	–	3.2
2	10.0	100	100.0	100.0	
3	25.0	250	260.0	104.0	
Gypsum – Delčevo					
1	–	–	<2.0	–	0.9
2	10.0	0.10	100.0	100.0	
3	25.0	0.25	250.0	100.0	
Gypsum – Probištip					
1	–	–	<2.0	–	0.6
2	10.0	100.0	100.0	100.0	
3	25.0	250.0	250.0	100.0	

The content of Fe in investigated minerals ranges from 10 to 500 μg/g; of Zn is below limit of detection in Ca-minerals, from 1 to 100 μg/g in galena; of Mn ranges from 1 to 50 μg/g in galena and gypsum and from 1 to 250 mg/g in sphalerite and siderite. The detection limit of the method was found to be 2 $\mu g \cdot g^{-1}$ for Zn and 5 $\mu g \cdot g^{-1}$ for Mn and Fe. The obtained values for the content of some of the investigated elements in galena and sphalerite are in agreement with those of Serafimovski et al. (1997).

Table 4

The content of manganese in galena, sphalerite, siderite, aragonite and gypsum

Sample/Mineral	m_{Mn} (add.) µg	w_{Mn} (calc.) µg/g	w_{Mn} (found) µg/g	R %	ICP-AES µg/g
Sphalerite – Toranica					
1	–	–	4.33	–	–
2	100.0	5.33	5.21	97.7	
3	200.0	6.33	6.16	97.3	
Sphalerite – Zletovo					
1	–	–	3.60	–	3.70
2	100.0	4.6	4.65	101.1	
3	200.0	5.6	5.45	97.3	
Galena – Sasa					
1	–	–	0.032		0.032
2	10.0	0.13	0.11	100.0	
3	25.0	0.28	0.26	100.4	
Galena – Zletovo					
1	–	–	<0.005	–	0.005
2	10	0.1	0.1	100.0	
3	25	0.25	0.25	100.0	
Siderite					
1	–	–	221.0	–	241.1
2	100	270.9	274.5	101.3	
3	200	321.0	323.7	100.9	
Aragonite					
1	–	–	0.169	–	–
2	50	0.669	0.675	100.8	
3	100	1.165	1.165	100.0	
4	200	2.163	2.183	100.9	
Gypsum – Delčevo					
1	–	–	<0.005	–	0.004
2	50	0.5	0.5	100.0	
3	100	1.0	1.0	100.0	
4	200	2.0	2.0	100.0	
Gypsum – Debar					
1	–	–	<0.005	–	0.006
2	50	0.5	0.5	100.0	
2	100	1.0	1.0	100.0	
3	200	2.0	2.0	100.0	

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Резиме

ОПРЕДЕЛУВАЊЕ НА Zn, Mn И Fe ВО НЕКОИ МИНЕРАЛИ СО АТОМСКА АПСОРПЦИОНА СПЕКТРОМЕТРИЈА

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Клучни зборови: железо; манган; цинк; атомска апсорпциона спектрометрија; сфалерит; галенит; сидерит; арагонит; гипс

Предложен е метод за определување на Fe, Mn и Zn со пламена атомска апсорпциона спектрометрија во различни сулфидни (галенит и сфалерит), карбонатни (сидерит, арагонит) и сулфатни (гипс) минерали. Испитувањето на влијанијата на матрицата покажа дека е можно директно определување на Fe, Mn и Zn од раствори добиени со растворање на минералите во смеси од киселини (HCl и HNO_3), освен во случајот на определувањето на Mn во калциумови матрици. Утврдено е дека присуството на калциумот доведува до намалување на апсорбанцата на Mn. Постапките се потврдени со методот на стандарден додаток и со споредба на резултатите со оние добиени со примена на атомската емисиона спектрометрија со индуктивно спрегната плазма. Утврдено е дека границата на детекција изнесува 2 μg/g за Zn, а 5 μg/g за Mn и Fe. Испитуваните минерали потекнуваат од различни рудници од Република Македонија.