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### AAS AND AES-ICP DETERMINATION OF TRACE ELEMENTS IN SOME IRON MINERALS

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#### Abstract

Different trace elements (Ag, Cd, Co, Cr, Mn, Ni, Pb and Zn) in some iron minerals were determined by flame (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) and by atomic emission spectrometry with induced coupled plasma (AES-ICP). To avoid the interference of iron, a method for extraction of iron and determination of investigated elements in inorganic phase was proposed. Iron was extracted by isoamyl acetate in HCl solution. Inorganic layer was evaporated and the residue was dissolved in 2 mol·dm<sup>-3</sup> HNO<sub>3</sub>, in order to eliminate the interferences of chlorides. The procedure was verified by the method of standard additions. The trace elements determination and the recovery show that satisfactory results were obtained. The determination of investigated elements was also performed for standard reference iron ore samples. Investigated minerals: hematite (Fe<sub>2</sub>O<sub>3</sub>), limonite (FeO·OH), magnetite (FeO·Fe<sub>2</sub>O<sub>3</sub>), marcasite (FeS<sub>2</sub>), pyrite (FeS<sub>2</sub>), siderite (FeCO<sub>3</sub>) and vivianite [Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O], originate from various localities from the Republic of Macedonia.

#### Introduction

The investigation of purity of iron minerals is very important because of their utilization for iron and steel production. There are a number of investigations concerning the determination of trace elements in similar geological samples by atomic absorption spectrometry<sup>1</sup>. Some authors have investigated the possibility of the AAS determination of these elements directly from the sample solution<sup>2-4</sup>. Thereby, the influence of interfering elements in the electrothermal AAS (ETAAS) determination has been of particular interest. To overcome such interferences, the addition of different matrix modifiers or the separation and concentration methods for determination of investigated elements were suggested<sup>5-8</sup>. To avoid potential interference of iron as matrix element on the absorption of investigated elements, separation of the iron by extraction<sup>9,10</sup> or by precipitation of iron<sup>11</sup> was suggested.

In this work we proposed a method for separation of the chloride complex of Fe by simple and rapid extraction into isoamyl acetate which effectively eliminates potential interference of Fe. Isoamyl acetate was used as a new ligand and organic solvent because it is very selective for iron extraction in the presence of another elements, except in the case of TI<sup>8,12</sup>. Investigated elements (Ag, Cd, Co, Cr, Mn, Ni, Pb and Zn) remain in the aqueous layer and they are analyzed by FAAS and Zeeman ETAAS and by atomic emission spectrometry with inductive coupled plasma (AES-ICP).

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\* Editorial note: Recognized by Greece as FYROM

## Experimental

### Instrumentation

A Varian SpectrAA 640Z Zeeman electrothermal atomic absorption spectrophotometer with a Varian PSD-100 Autosampler and Varian SpectrAA 880 with deuterium correction (for flame determination) were used. Hollow cathode lamps were used as a source. Argon was used as a cleaning gas and 10  $\mu$ l of samples were introduced into graphite tube. Mn and Zn were analyzed by flame AAS and Ag, Cd, Co, Cr, Ni and Pb by ETAAS. Operating conditions for the ETAAS determination are given in Table 1. Inductively coupled plasma-atomic emission spectrometric (ICP-AES) determinations were performed by ICP-AES spectrometer Varian Model Liberty 110. Optimal instrumental parameters are given in Table 2.

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

Parameter	Ag	Cd	Co	Cr	Ni	Pb
Drying						
Temperature/°C; time/s	120; 55	120; 55	120; 55	120; 55	120; 55	120; 55
Pyrolysis						
Temperature/°C; time/s	600; 20	300; 20	750; 8	1000; 3	800; 8	400; 8
Atomizing						
Temperature/°C; time/s	2000; 3	2000; 3	2300; 3	2500; 3	2400; 3	2100; 3
Cleaning						
Temperature/°C; time/s	2400; 2	2400; 2	2400; 2	2600; 2	2500; 2	2200; 2

**Table 2.** Instrumentation and operating conditions for ICP-AES system

<b>ICP system</b>	Varian, Liberty 110
<b>RF Generator</b>	
Operating frequency	40.68 MHz
Coupling	Direct Serial Coupling - DISC ( $\approx$ 70 % efficiency)
R. f. power	Auto tune, 1.0 kW
<b>Spectrometer</b>	
Optical arrangement	Czerny Turner 0.75 m focal length
Grating	Holographic
Groove Density	1800 Lines/mm
Size	100 $\times$ 90 mm
Spectral Resolution	18 pm
Background corrector	dynamic
<b>Sample Introduction area</b>	
Plasma Ar flow rate	15 l/min
Auxiliary Ar flow rate	1.5 l/min
Nebulizer Ar flow rate	2 l/min
Spray Chamber	Inert Sturman-Masters
Sample flow rate	2 ml/min
Peristaltic pump	25 rollers, 1 turn/min increment
Integration time	5 s, Direct Reading Instrument

### Reagents and Samples

All reagents and standards were of analytical grade. The mass concentration of stock solutions of Pb, Co, Ni, Cr, Mn and Zn were 1 mg/l, and from these solutions other diluted solutions were prepared. The investigated minerals (hematite, limonite, magnetite, marcasite, pyrite, siderite and vivianite) originate from different localities from the Republic of Macedonia.

### Procedures

*Pyrite, marcasite and vivianite.* 0.1-0.5 g of powdered sample was dissolved in 5 ml conc. HCl and 5 ml conc. HNO<sub>3</sub>. A few drops of H<sub>2</sub>O<sub>2</sub> were added and the solution evaporated to near dryness. The residue was dissolved with 50 ml of 8 mol/l HCl. After dissolution of the mineral samples, the solution was transferred into a separatory funnel. Then 5 ml isoamyl acetate were added and the mixture was shaken for 1 min. This operation was repeated 4 times. To avoid interferences of chlorides, inorganic layer was evaporated and the residue was dissolved in 5 ml of 2 mol/l HNO<sub>3</sub>.

*Hematite, limonite and magnetite.* 0.1-0.5 g of powdered sample was dissolved in 12 ml aqua regia. The same procedure was followed as described before.

*Siderite.* 0.1-0.5 g of powdered sample was dissolved in 5 ml conc. HCl, 1 ml HNO<sub>3</sub> and 1 ml H<sub>2</sub>O<sub>2</sub>. The solution was evaporated to dryness, and then the same procedure as described for pyrite, marcasite and vivianite was followed.

### Result and Discussion

One of the major problems in ETAAS and AES-ICP is matrix interference. Therefore, the interference of Fe (as a matrix element of the minerals studied), on the other elements was investigated. Results show that Fe tends to decrease absorbance of the most of the elements. Therefore, a method for elimination of iron by extraction and determination of investigated elements in inorganic phase, in order to avoid the interference of iron, was proposed. In this case an extraction of iron as matrix elements was performed using isoamyl acetate as ligand and solvent<sup>8,12,13</sup>

Optimization of extraction procedure was performed. Operating factors such as the concentration of HCl, amount of Fe present, number of extractions and the optimum ratio of volume of organic to inorganic phase, were determined. It was found that quantitative extraction of Fe was obtained when the concentration of HCl is over 8 mol/l. The optimal volume ratio between organic and inorganic phases was found to be 1:5. To avoid interferences of chlorides on one hand, and to concentrate the investigated elements, on the other hand, inorganic layer was evaporated and the residue was dissolved in 5 ml of 2 mol/l HNO<sub>3</sub>.

The used method was verified by the method of standard additions. An exact amount of standard solutions with a known concentration of investigated elements was added to mineral samples. The obtained recoveries for Ag (89.1-100.3 %), Cd (95.4-100.1 %), Co (97.5-102.4 %), Cr (100.1-101.7 %), Mn (97.3-104.1 %), Ni (97.0-100.2 %), Pb (99.7-104.6 %), Zn (98.9-103.3 %) show that satisfactory results were found. It was also noticed that a part of copper was extracted with isoamyl acetate and the recovery was below 80 %. The determination of these elements was also performed for iron ore standard reference sample (JSS 820-2) and the results show that the concentration for Pb, Co, Cr, Ni and Mn using the proposed method are very similar to those provided for the certified sample.

Results from the determination of investigated elements in iron minerals taken from different localities in the Republic of Macedonia are given in Table 3. As it can be seen, the content of Mn and Zn in the most of the minerals (especially those taken from the Pb-Zn mines of Sasa and Zletovo) is very high, indicating the high contamination of these Fe-minerals with Zn- and Mn-minerals. Higher content of Ag, Cd and Pb in pyrite from Sasa and siderite from Zletovo also indicates the contamination of minerals in these localities. Extremely high content of Zn (175.3 mg/g) shows that this mineral sample is mixed with sphalerite (ZnS). It was also found that the content of Mn is very high in siderite samples from Zletovo deposit, which is in accordance with our previous data about the appearance of Mn minerals with iron minerals<sup>14</sup>.

### Conclusion

It was shown that lead, cobalt, chromium, nickel, manganese and zinc could be determined by both flame and electrothermal atomic absorption spectrometry in different iron minerals after extraction separation of iron with isoamyl acetate from 8 mol/L HCl media.

**Table 3.** Results from the determination of investigated elements in different iron mineral samples.

No	Mineral	Locality (mine)	Mn mg/g	Zn mg/g	Ag µg/g	Cd µg/g	Co µg/g	Cr µg/g	Ni µg/g	Pb µg/g
1	Pyrite	Bučim	0.467	0.249	0.13	0.52	17.3	9.2	20.0	0.075
2	Pyrite	Sasa	2.478	175.3	29.0	142.0	<0.01	58.9	106.0	4.372
3	Siderite-1*	Zletovo	139.0	0.990	31.0	2.33	<0.01	12.0	0.87	0.181
4	Siderite-2*	Zletovo	157.8	1.105	42.5	2.92	<0.01	5.04	9.46	0.235
5	Siderite-3*	Zletovo	138.6	7.728	34.7	11.5	<0.01	0.93	8.54	1.135
6	Limonite	Damjan	1.078	0.288	0.74	0.19	<0.01	5.13	9.4	0.123
7	Limonite	Pehčevo	0.059	0.099	<0.05	0.10	1.77	66.6	7.95	0.118
8	Magnetite	Damjan	1.175	0.218	11.5	<0.05	10.3	30.5	21.0	0.011
9	Hematite	Damjan	0.083	0.138	<0.05	<0.05	0.53	18.2	26.3	0.233
10	Marcasite	Alšar	0.098	0.157	2.86	1.34	51.4	0.93	14.4	0.013
11	Vivianite	Pelagonija	14.43	0.063	0.31	0.20	1.06	21.7	29.2	0.100

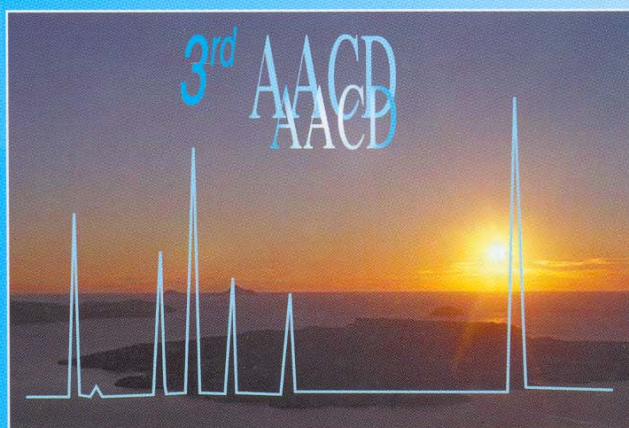
\* Siderite-1 is white colored shell formed; siderite-2 is brown shell formed and siderite-3 is white and kidney formed mineral

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