

## LIQUID-LIQUID EXTRACTION AND DETERMINATION OF TRACE ELEMENTS IN IRON MINERALS BY ATOMIC ABSORPTION SPECTROMETRY

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**Abstract:** Various trace elements (cadmium, chromium, cobalt, nickel, manganese) in some iron minerals were determined by flame (FAAS) and electrothermal atomic absorption spectrometry (ETAAS). The studied minerals were chalcopyrite (CuFeS<sub>2</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>) and pyrite (FeS<sub>2</sub>). To avoid the interference of iron, a method for liquid-liquid extraction of iron and determination of investigated elements in the inorganic phase was proposed. Iron was extracted by diisopropyl ether in hydrochloride acid solution and the extraction method was optimized. Some parameters were obtained to be significantly important: Fe mass in the sample should not exceed 0.3 g, the optimal concentration of HCl should be 7.8 mol l<sup>-1</sup> and ratio of the inorganic and organic phase should be 1:1. The procedure was verified by the method of standard additions and by its applications to reference standard samples. The investigated minerals originate from various mines in the Republic of Macedonia.

**Key words:** cadmium; chromium; cobalt; nickel; manganese; chalcopyrite; hematite; pyrite; atomic absorption spectrometry

### INTRODUCTION

During a long geological period it is not possible to obtain absolutely pure minerals without any contamination, which means that most minerals contain extraneous substances that change some of their characteristics. There are a number of elements that are quite easily interchangeable, causing the transformation of one mineral into another.

Iron minerals are very important because of their utilization for iron and steel production. Atomic absorption spectrometry (AAS) is one of the most used analytical techniques for the investigation of the purity of the iron minerals (Stafilov, 2000). Because iron as a matrix element is present in the solutions obtained after dissolution of iron minerals, interferences could be expected (Stafilov, 2000). Therefore, various separation methods were suggested to overcome such interferences (Eidecker and Jackwerth, 1988; Kabil et al., 1996; Lazaru and Stafilov, 1998; Zendelovska and Stafilov, 2001). To avoid potential interference of iron

as matrix element on the absorption of investigated elements, some authors have suggested separation of the iron by extraction with methylisobutyl ketone (Chen et al., 1992), or with di(2-ethylhexyl) phosphoric acid into kerosine (Agatzini et al., 1986), as well as by isoamyl acetate (Zendelovska & Stafilov, 2001; Stafilov & Zendelovska, 2002; Taseska et al., 2005) or by precipitation of iron (Agatzini et al., 1986).

In this work we proposed a method for separation of the chloride complex of iron by simple and rapid extraction into diisopropyl ether, which effectively eliminates the potential interference of iron. Trace elements investigated (Co, Cd, Cr, Mn, Ni) remain in the aqueous layer and they are analyzed by flame AAS (FAAS) and Zeeman electrothermal AAS (ETAAS). The minerals investigated (hematite, pyrite and chalcopyrite) originate from different mines in the Republic of Macedonia.

## EXPERIMENTAL

*Instrumentation*

A Varian SpectrAA 640 Z Zeeman electrothermal atomic absorption spectrometer with a Varian PSD-100 Autosampler and flame atomic absorption spectrometer Thermo Model Solaar 2 with deuterium correction were used. Hollow cathode lamps were used as a source. Operating conditions for the determination of Co, Cr, Cd, Mn, and Ni are given in Tables 1 and 2.

Table 1

*Instrumental parameters for determination of Cd, Co, Cr, Mn and Ni by flame AAS*

Element	Parameters		
	Wavelength nm	Slit nm	Lamp current mA
Cd	228.8	1.0	4
Ni	232.0	0.2	4
Cr	357.9	0.2	7
Co	240.7	0.2	7
Mn	279.5	0.2	5
Gas mixture	Acetylene/air		

Table 2

*Optimal parameters for Cd, Co, Cr, Mn and Ni determination by Zeeman ETAAS*

Parameters	Co	Ni	Mn	Cr	Cd
Wavelength/nm	242.5	232.0	279.5	357.9	228.8
Slit/nm	0.2	0.2	0.2	0.5	0.5
Lamp current/mA	7.0	4.0	10.0	5.0	4
Calibration mode	Absorbance, peak height				
Background correction	Zeeman				
Drying					
Temperature / °C	85; 95; 120	85; 95; 120	85; 95; 120	85; 95; 120	85; 95; 120
Time / s	5; 40; 10	5; 40; 10	5; 40; 10	5; 40; 10	5; 40; 10
Pre-treatment					
Temperature / °C	750	800	700	1000	250
Ramp time / s	5	5	10	5	5
Hold time / s	20	20	20	20	20
Atomization					
Temperature / °C	2300	2400	2400	2600	1800
Ramp time / s	1	1	1	1	1
Hold time / s	2	2	2	2	2
Cleaning					
Temperature / °C	2300	2400	2400	2600	1800
Hold time / s	2	2	2	2	2
Gas	Argon				

*Reagents and samples*

All reagents and standards were of analytical grade. Stock solutions of Cd, Co, Cr, Mn and Ni are delivered by Solution Plus Inc. (USA) with the concentration of 1 mg ml<sup>-1</sup>. They were used for preparing other diluted solutions. Mineral samples were collected from different mines in Republic of Macedonia: hematite (Damjan mine), pyrite (Bućim mine) and chalcopyrite (Bućim mine).

*Procedures*

Pyrite: 0.1–0.5 g of powdered sample was dissolved in 5 ml concentrated HCl and 5 ml concentrated 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 7.8 mol l<sup>-1</sup> HCl. After dissolution of the mineral samples, the solution was transferred into a separatory funnel. Then 10 ml of diisopropyl ether were added and the mixture was shaken for 1 min. To avoid interferences

of chlorides, the inorganic layer was evaporated and the residue was dissolved in 5 ml of 2 mol l<sup>-1</sup> HNO<sub>3</sub>.

**Hematite:** 0.1–0.5 g of powdered sample were dissolved in 12 ml aqua regia. The same procedure described for pyrite was followed.

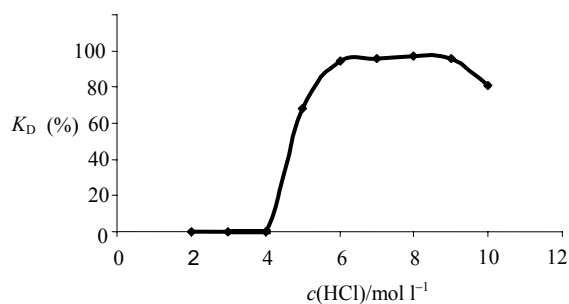
**Chalcopyrite:** 0.1–0.5 g of powdered sample were dissolved in 6 ml of concentrated HCl, 2 ml concentrated HNO<sub>3</sub> and few drops of concentrated H<sub>2</sub>O<sub>2</sub>. The solution is evaporated to dryness and the residue dissolved in 2 ml of concentrated H<sub>2</sub>SO<sub>4</sub>, 1 ml concentrated HNO<sub>3</sub> and about 100 ml redistilled water. The Pt-electrode was employed

for copper electrolysis for 45 min at 2 V and 3–4 A. After washing the Pt-electrode with redistilled water, copper was dissolved with HNO<sub>3</sub> (1+2) and determined by mass difference (Taseska et al., 2005). After electrolysis of copper, the solution was evaporated to 10 ml, transferred into a separatory funnel adding HCl in order to obtain a concentration of 7.8 mol l<sup>-1</sup>. After that a 10 ml volume of diisopropyl ether is added and the obtained mixture is shaken for 1 min. After the phase separation the inorganic part was transferred into a glass beaker, evaporated and the residue dissolved in 5 ml of 2 mol l<sup>-1</sup> HNO<sub>3</sub>.

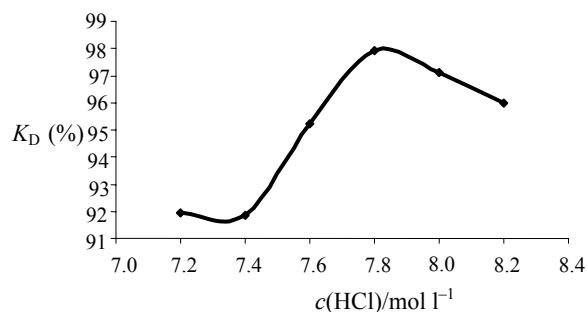
## RESULTS AND DISCUSSION

The mayor problem in atomic absorption spectrometry is matrix interference. It was found that iron tends to decrease absorbance of some trace elements (Co and Cr) or to increase the absorbance of Ni at high concentration (Stafilov and Zendelovska, 2002). To avoid interference of iron, a method for the extraction of iron and determination of the elements investigated in the inorganic phase was proposed. In this case a liquid-liquid extraction of iron as matrix elements was performed using diisopropyl ether.

The extraction method was optimized. 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. As can be seen in Figs. 1 and 2, quantitative extraction (over 98 %) of iron was achieved when the concentration of HCl was over 6 mol l<sup>-1</sup>. For a better recovery of iron (99 %), a concentration of 7.8 mol l<sup>-1</sup> of HCl was used in this procedure (Fig. 2).



**Fig. 1.** Effect of HCl concentration on the extraction recovery of iron (from 2 to 10 mol l<sup>-1</sup>)



**Fig. 2.** Effect of HCl concentration on the extraction recovery of iron (from 7.2 to 8.2 mol l<sup>-1</sup>)

It was also determined that the volume ratio of 1:1 between the organic and inorganic phases was optimal for iron extraction (Table 3) and that a mass of up to 0.3 g of iron is a maximum one in mineral sample (Table 4).

In order to avoid interferences of chlorides, and to concentrate the investigated elements, the inorganic layer was evaporated and the residue was dissolved in 5 ml of 2 mol l<sup>-1</sup> HNO<sub>3</sub>.

**Table 3**

*Influence of the organic and inorganic phases volume ratio in 7.8 mol l<sup>-1</sup> HCl media*

<i>V</i> (inorganic) / ml	10	25	50	10	25	50
<i>V</i> (organic) / ml	5	5	5	10	10	10
Recovery (%)	96.6	94.52	69.1	98.2	97.0	92.0

Table 4  
Influence of iron mass on the distribution coefficient,  $K_D$

		One-step extraction				
$m(\text{Fe}) / \text{mg}$		100	200	300	400	500
$K_D (\%)$		97.5	97.98	97.3	95.9	92.7
		Two-step extraction				
$m(\text{Fe})/\text{mg}$		100	200	300	400	500
$K_D (\%)$		99.6	99.9	99.8	99.8	99.7

The 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 result of Co, Cr, Cd, Mn and Ni determinations and the recovery levels are given in Table 5 showing that satisfactory results were obtained.

Table 5  
Determination of Cd, Co, Cr, Mn and Ni, in iron minerals and results of recovery tests

Sample	$m_{\text{Metal}}$ (added) $\mu\text{g}$	Metal content (calculated) $\mu\text{g g}^{-1}$	Metal content (found) $\mu\text{g g}^{-1}$	Recovery %
Cd				
Chalcopyrite	–	–	62.10	–
	5	112.1	109.75	97.9
	10	160.39	152.1	94.8
Co				
Chalcopyrite	–	–	56.41	–
	1	66.01	62.26	94.3
Cr				
Chalcopyrite	–	–	23.69	–
	5	71.72	63.83	89
Hematite	–	–	33.0	–
Pyrite	–	–	11.0	–
Mn				
Chalcopyrite	–	–	15821.5	–
	5	16231.8	17363.5	106.9
	10	16280.1	17133.9	105.2
Hematite	–	–	99.0	–
Pyrite	–	–	350.0	–
Ni				
Chalcopyrite	–	–	41.35	–
	10	137.65	132.85	96.5
Hematite	–	–	52.0	–
Pyrite	–	–	139.0	–

The determination of these elements was also performed for three referent iron ore standard samples: JSS 820-2, JSS 804-1 and JSS 805-1 (Iron and Steel Institute of Japan). The results of measured and certified values are given in Table 6. As can be seen, the concentration for Cr, Mn and Ni using the proposed method are very similar to those provided for the certified samples.

Table 6  
Determination of Cr, Mn and Ni in referent standard samples

Element	Referent standard samples			
	Certified/Found	JSS 804-1	JSS 805-1	JSS 820-2
Cr	Certified (%)	–	–	0.0020
	Found (%)	–	–	0.0019
Mn	Certified (%)	0.0160	0.250	–
	Found (%)	0.0141	0.242	–
Ni	Certified (%)	0.0028	–	0.0030
	Found (%)	0.0031	–	0.0030

A comparison of the contents of Cd, Co, Cr, Mn and Ni obtained in this work (Table 5) with other results for the corresponding iron minerals from different localities from Macedonia (Makreski et al., 2002; Stafilov & Zendelovska, 2002; Makreski et al., 2004; Taseska et al., 2005; Jaćimović et al., 2005) was made (Table 7). It was found that the obtained values are close to those obtained by different techniques: AAS (Makreski et al., 2002; Stafilov & Zendelovska, 2002; Taseska et al., 2005), atomic emission spectrometry with inductively coupled plasma, AES-ICP (Makreski et al., 2002) or by  $k_0$ -instrumental neutron activation analysis,  $k_0$ -INAA (Makreski et al., 2004; Jaćimović et al., 2005). It was also found that the content of Cd, Co, Cr, Mn and Ni is related to the origin of the minerals and the mineralization of its locality. Therefore, the contents of Cd in pyrite and chalcopyrite from Sasa are evidently higher compared to the corresponding values for the mineral samples collected in the Bućim locality (Aleksandrov, 1998). On the other hand, the high content of Co in hematite from Ržanovo (two different samples) is related to the abundance of Co in Fe/Ni mineralization (Boev & Stojanov, 1985; Boev & Janković, 1996).

Table 7

Comparison of results obtained for Cd, Co, Cr, Mn and Ni in investigated iron minerals with literature data (mg/kg)

Mineral	Locality	Elements					Reference
		Cd	Co	Cr	Mn	Ni	
Pyrite	Bučim	–	–	11.0	350	139	This work
	Bučim	< 5	18.1	9.24	–	–	Jaćimović et al., 2005
	Bučim	0.52	17.3	9.2	467	20.0	Makreski et al., 2002
	Bučim	–	36.8	11.6	470	29.3	Stafilov & Zendelovska, 2002
	Sasa	142.0	< 0.01	58.9	2478	106.0	Makreski et al., 2002
Chalcopyrite	Bučim	62.1	56.4	23.69	15821	41.35	This work
	Bučim	54.9	19.5	80.3	661.1	34.86	Taseska et al., 2005
	Sasa	90.1	28.9	30.0	–	–	Jaćimović et al., 2005
Hematite	Damjan	–	–	33	99	52	This work
	Damjan	< 4	3.64	29.3	–	–	Jaćimović et al., 2005
	Damjan	< 0.05	0.53	18.2	83	26.3	Makreski et al., 2002
	Damjan	0.9	3.9	–	–	–	Makreski et al., 2004
	Damjan	–	1.79	16.4	98	43.37	Stafilov & Zendelovska, 2002
	Ržanovo	–	–	–	1860	–	Stafilov & Zendelovska, 2002
	Ržanovo	< 0.05	390	–	–	–	Makreski et al., 2004

## CONCLUSION

It was shown that cadmium, chromium, cobalt, manganese and nickel could be determined by both flame and electrothermal atomic absorption spectrometry in different iron minerals after liquid-liquid extraction of iron with diisopropyl ether from 7.8 mol l<sup>-1</sup> HCL media.

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## Резиме

## ТЕЧНО-ТЕЧНА ЕКСТРАКЦИЈА И ОПРЕДЕЛУВАЊЕ НА ЕЛЕМЕНТИ ВО ТРАГИ ВО МИНЕРАЛИ НА ЖЕЛЕЗО СО АТОМСКА АПСОРПЦИОНА СПЕКТРОМЕТРИЈА

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**Клучни зборови:** кадмиум; хром; никел; манган; халкопирит; хематит; пирит;  
атомска апсорпциона спектрометрија

Определена е содржината на елементи во траги (кадмиум, хром, кобалт, манган) во некои минерали на железо со примена на пламена и електротермичка атомска апсорпциона спектрометрија. Испитувани се следните минерали: халкопирит (CuFeS<sub>2</sub>), хематит (Fe<sub>2</sub>O<sub>3</sub>) и пирит (FeS<sub>2</sub>). За да се избегне влијанието на железото врз апсорбанцата на елементите во траги, извршено е оптимирање на методот за течно-течна екстракција на железото. Железото е екстрахирано со

диизопропилетер во раствор од хлороводородна киселина. Оптимирани се важните параметри на екстракцијата: масата на Fe во примерокот да не надминува 0,3 g, оптималната концентрација на HCl да изнесува 7,8 mol l<sup>-1</sup>, а односот на неорганската и органската фаза да е 1:1. Постапката е верифицирана со методот на стандарден додаток и со примена на сертификирани материјали. Испитуваните минерали потекнуваат од различни локалитети во Република Македонија.