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Determination of Trace Elements in Iron Minerals by Atomic Absorption Spectrometry

Trajče STAFILOV*, Dragica ZENDELOVSKA
Institute of Chemistry, Faculty of Science,
St. Cyril and Methodius University,
P.O. Box 162, 91001 Skopje-MACEDONIA
e-mail: trajcest@iunona.pmf.ukim.edu.mk

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A method for the determination of lead, cobalt, nickel, chromium, zinc and manganese in iron minerals siderite ($FeCO_3$), hematite (Fe_2O_3), pyrite and marcasite (FeS_2)by flame and Zeeman electrothermal atomic absorption spectrometry (ETAAS) was developed. Interferences were investigated by measuring the absorbance of the elements investigated in series of samples with varying mass ratios of the elements investigated and iron as the potential interfering element. It was found that there was no interference in the determined mass ratios of iron on the absorbance of Mn and Zn and that they could be directly analyzed by flame and electrothermal atomic absorption spectrometry. However, iron tends to decrease the absorbance of Co, Cr, and Pb and to increase the absorbance of Ni. Therefore, to avoid the interference of iron, a method for extraction of iron and determination of investigated elements in the inorganic phase was proposed. Iron was extracted by isoamyl acetate in hydrochloride acid solution. Optimization of the extraction procedure was performed. The procedure was verified by the method of standard additions and by its application to reference standard samples. The minerals investigated originate from different mines in the Republic of Macedonia. It was found that the detection limits of the method (calculated as 3 SDs of the blank) are 10 ng·g^{-1} for Ni and Cr and 30 ng·g^{-1} for Pb and Co, determined by Zeeman ETAAS, and 0.10 μg·g^{-1} for Zn and 0.25 μg·g^{-1} for Mn, determined by flame AAS.

Key Words: iron minerals, trace elements, lead, cobalt, nickel, chromium, zinc, manganese, determination, atomic absorption spectrometry

Introduction

Minerals are natural occurring inorganic substances with a relatively constant chemical composition and fairly well defined physical properties. During long geological periods 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, with the result that one mineral may grade into another.

*Correspondence

Therefore, there are many reasons to analyze trace elements in different minerals: to determine the purity of minerals, and to determine the presence of very rare and important elements which could be extracted and used to obtain data which give very important information on the geology of the mines and mineral localities.

The investigation of the 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 elements investigated in similar geological samples by flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS)[1]. Some authors have investigated the possibility of the determination of these elements directly from the sample solution, by FAAS[2−6], or by ETAAS[6−11]. Also, the influence of interfering elements was of particular interest in the flame or electrothermal AAS determination and, to overcome such interferences, the addition of different matrix modifiers or the separation and concentration methods for the determination of the elements investigated were suggested[12−22]. To avoid the potential interference of iron as a matrix element on the absorption of investigated elements, some authors have suggested separation of the iron by extraction with isobutyl acetate[23], methylisobutyl ketone[24−26], di(2-ethylhexyl) phosphoric acid into kerosine[27] or 2-hexylpyridine into benzene[28] or by the precipitation of iron[27,29].

In this work we proposed a method for separation of the chloride complex of iron by simple and rapid extraction into isoamyl acetate, which effectively eliminates the potential interference of iron. Isoamyl acetate was used as a new ligand and organic solvent because it is very selective for iron extraction in the presence of other elements, except in the case of thallium[22,30]. The elements investigated (Pb, Co, Cr, Ni, Mn and Zn) remain in the aqueous layer and they are analyzed by FAAS and Zeeman ETAAS. The minerals investigated (siderite, hematite, pyrite and marcasite) originate from different mines in the Republic of Macedonia.

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. Operating conditions for the determination of Pb, Co, Ni, Cr, Mn and Zn are given in Tables 1 and 2.

Table 1. Instrumental parameters for determination of Pb, Ni, Cr, Co, Mn, Cu and Zn by flame AAS

Element	Parameters		
	Wavelength, nm	Slit, nm	Lamp current, mA
Pb	283.3	1.0	5
Ni	232.0	0.2	4
Cr	357.9	0.2	7
Co	240.7	0.2	7
Mn	279.5	0.2	5
Zn	213.9	1	5
Gas mixture	Acetylene/air		

Table 2. Optimal parameters for Co, Ni, Pb and Cr determination by Zeeman ETAAS

Parameters	Co	Ni	Pb	Cr
Wavelength, nm	242.5	232.0	283.3	357.9
Slit, nm	0.2	0.2	0.5	0.5
Lamp current, mA	7.0	4.0	5.0	5.0
Calibration mode	Absorbance, peak height			
Aliquot injected into graphite furnace	10 μL			
GAS	Argon			

Step	Temperature (°C)	Time (s)	Gas flow (l/min)
		Co	
1	85	5	3
2	95	40	3
3	120	10	3
4	750	5	3
5	750	1	3
6	750	2	0
7	2300	1	0
8	2300	2	0
9	2400	2	3
		Ni	
1	85	5	3
2	95	40	3
3	120	10	3
4	800	5	3
5	800	1	3
6	800	2	0
7	2400	1	0
8	2400	2	0
9	2500	2	3
		Pb	
1	85	5	3
2	95	40	3
3	120	10	3
4	400	5	3
5	400	1	3
6	400	2	0
7	2100	1	0
8	2100	2	0
9	2200	2	3
		Cr	
1	85	5	3
2	95	40	3
3	120	10	3
4	1000	5	3
5	1000	1	3
6	1000	2	0
7	2500	1	0
8	2500	2	0
9	2600	2	3

Reagent and samples

All reagents and standards were of analytical grade. Stock solutions of Pb, Co, Ni, Cr, Mn and Zn were prepared by dissolving $Pb(NO_3)_2$, $CoCl_26H_2O$, Ni metal, K_2CrO_4, $MnCl_2$ and Zn metal. The mass concentration of solutions was 1 $mg{\cdot}L^{-1}$, and from these solutions other diluted solutions were prepared. Mineral samples were collected in different mines in Republic of Macedonia: hematite-1 (Damjan mine), hematite-2 (Rzanovo mine), siderite (Zletovo mine), marcasite (Alsar mine) and pyrite (Bucim mine).

Procedures

(a) Pyrite and marcasite. 0.1-0.5 g of powdered sample of pyrite or marcasite was dissolved in 5 mL concentrated HCl and 5 mL concentrated HNO_3. A few drops of H_2O_2 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 10 mL of isoamyl acetate was added and the mixture was shaken for 1 minute. To avoid interferences of chlorides, the inorganic layer was evaporated and the residue was dissolved in 5 mL of 2 mol/L HNO_3.

(b) Siderite. 0.1-0.5 g of powdered sample of siderite was dissolved in 5 mL concentrated HCl, 1 mL HNO_3 and 1 mL H_2O_2. The solution was evaporated to dryness, and then the same procedure was followed as described for pyrite and marcasite.

(c) Hematite. 0.1-0.5 g of powdered sample of hematite was dissolved in 12 mL aqua regia. The same procedure was followed as described for the other minerals.

Results and Discussion

One of the major problems in electrothermal atomic absorption spectrometry (ETAAS) is matrix interference. Therefore, the interference of iron, as a matrix element of the minerals studied, on the lead, cobalt, nickel, chromium, manganese and zinc determination was investigated. Series of solutions with the same concentrations of these elements and different concentration of interfering element were tested to check if iron caused any interference in the determination of the elements investigated. This influence was investigated by measuring the absorbance of the elements investigated in a series of samples with varying concentrations of iron. The concentrations of these elements were similar to the concentrations in the sample solutions.

The results show that there is no interference in the determined mass ratios (similar to those in the minerals investigated) of the matrix on the absorbance of Mn and Zn. This means that Zn and Mn could be determined directly from the solution obtained by mineral dissolution or after the extraction of Fe. Because of the relatively high concentration of these two elements in the minerals investigated they were analyzed by flame AAS. However, iron tends to decrease the absorbance of Co, Cr and Pb and increase the absorbance of Ni at high concentration (Fig. 1). These interferences are mainly due to the high quantity of iron present in the graphite tube, preventing complete atomization of the elements investigated during the atomization step (Co, Cr, Pb) or affecting by spectral interferences overlapping the resonance line of Ni by reaching the atomic spectrum of iron.

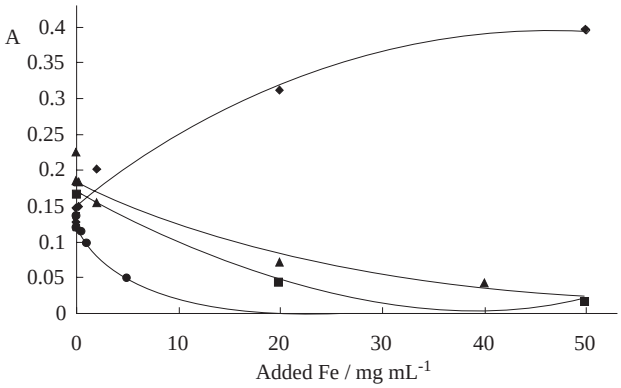

Figure 1. Influence of iron on Pb (Δ), Co (□), Cr (●) and Ni (◊) absorbance in ETAAS determination (concentration of Pb, Co, Cr and Ni is 20 ng/mL)

Therefore, to avoid the interference of iron, we propose a method for the elimination of iron and the determination of the elements investigated in the inorganic phase. In this case an extraction of iron as matrix elements was performed using isoamyl acetate as the ligand and solvent[22,30,31].

Optimization of the 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. As can be seen in Fig. 2, quantitative extraction (over 95%) of iron was achieved when the concentration of HCl was over 7 mol·L^{-1}. For a better recovery of iron (99%), a concentration of 8 mol·L^{-1} of HCl was used in this procedure. It was also determined that the volume ratio of 1:5 between the organic and inorganic phases was optimal for iron extraction and that a mass of up to 0.5 g of iron mineral is a maximal mass of mineral sample.

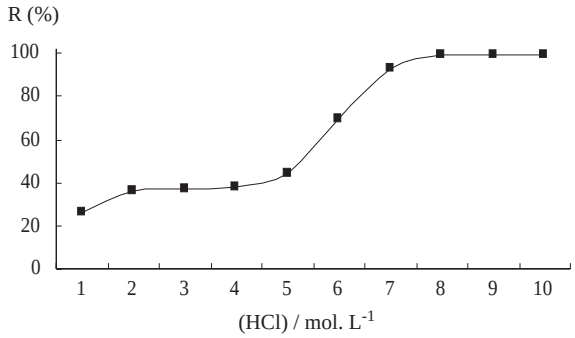

Figure 2. Effect of HCl concentration on the extraction recovery (R) of iron

To avoid interferences of chlorides from one, and to concentrate the investigated elements, the inorganic layer was evaporated and the residue was dissolved in 5 mL of 2 mol·L^{-1} HNO_3.

The method was verified by the method of standard additions for the elements investigated and minerals. An exact amount of standard solutions with a known concentration of investigated elements was added to mineral samples. The result of Pb, Co, Cr, Ni, Zn and Mn determinations and the recovery levels are given in Tables 3-8 and show that satisfactory results were obtained.

Table 3. Determination of Co in iron minerals and results of recovery tests

Sample	Co(added)/μg g^{-1}	Co(found)/μg g^{-1}	Co(calc.)/μg g^{-1}	Recovery (%)
		Siderite		
1	-	1.60	-	-
2	2.0	3.52	3.60	97.8
3	5.0	6.51	6.60	98.6
4	10.0	11.50	11.60	99.1
		Hematite 1		
1	-	1.79	-	-
2	5.0	6.79	6.79	100.0
3	10.0	11.76	11.79	99.7
		Marcasite		
1		32.12	-	-
2	23.0	54.46	55.12	98.8
3	46.0	77.91	78.12	99.7
4	92.0	124.7	124.12	100.5
		Pyrite		
1	-	36.76	-	-
2	23.0	59.44	59.76	99.4
3	46.0	83.29	82.76	100.6
4	92.0	128.3	128.76	99.6

Table 4. Determination of Cr in iron minerals and results of recovery tests

Sample	Cr(added)/μg g^{-1}	Cr(found)/μg g^{-1}	Cr(calc.)/μg g^{-1}	Recovery(%)
		Siderite		
1	-	7.98	-	-
2	2.0	10.05	9.98	100.7
3	5.0	13.03	12.98	100.4
4	10.0	18.00	17.98	100.1
		Hematite 1		
1	-	16.41	-	-
2	35.0	50.98	51.41	99.2
3	140.0	153.6	156.41	98.2
		Marcasite		
1	-	0.90	-	-
2	2.0	2.90	2.90	100.0
3	10.0	10.90	10.90	100.0
		Pyrite		
1	-	11.60	-	-
2	2.0	13.63	13.60	100.2
3	5.0	16.67	16.60	100.4

Table 5. Determination of Pb in iron minerals and results of recovery tests

Sample	Pb(added)/μg g^{-1}	Pb(found)/μg g^{-1}	Pb(calc.)/μg g^{-1}	Recovery (%)
		Hematite 1		
1	-	18.25	-	-
2	50.0	68.30	68.25	100.1
3	100.0	117.9	118.25	99.7
4	150.0	164.5	167.25	98.3
		Hematite 2		
1	-	97.60	-	-
2	50.0	145.5	147.6	98.6
3	150.0	241.9	247.6	97.7
		Marcasite		
1	-	12.55	-	-
2	50.0	62.50	62.55	99.9
3	100.0	112.4	112.55	99.8
		Pyrite		
1	-	25.70	-	-
2	50.0	75.55	75.7	99.8
3	100.0	124.5	125.7	99.0
4	150.0	171.6	175.7	97.7

Table 6. Determination of Ni in iron minerals and results of recovery tests

Sample	Ni(added)/μg g^{-1}	Ni(found)/μg g^{-1}	Ni(calc.)/μg g^{-1}	Recovery (%)
		Siderite		
1	-	10.27	-	-
2	5.0	15.43	15.27	101.0
3	10.0	20.20	20.27	99.65
		Hematite 1		
1	-	43.37	-	-
2	2.0	45.50	45.37	100.3
3	5.0	48.40	48.37	100.0
4	10.0	53.14	53.37	99.6
		Marcasite		
1	-	9.34	-	-
2	2.0	11.80	11.34	104.0
3	5.0	14.57	14.34	101.6
4	10.0	19.40	19.34	100.3
		Pyrite		
1	-	29.30	-	-
2	10.0	39.38	39.30	100.2
3	20.0	49.14	49.30	99.7

Table 7. Determination of Mn in iron minerals and results of recovery tests

Sample	Mn(added)/mg g^{-1}	Mn(found)/mg g^{-1}	Mn(calc.)/mg g^{-1}	Recovery (%)
		Hematite 1		
1	-	0.098	-	-
2	0.035	0.128	0.133	96.2
3	0.075	0.161	0.173	93.1
		Hematite 2		
1	-	1.86	-	-
2	0.18	1.91	2.04	93.6
3	0.36	2.01	2.22	90.5
		Marcasite		
1	-	96.5	-	-
2	50.0	134.8	146.5	92.1
3	100.0	182.0	196.5	92.6
		Pyrite		
1	-	0.47	-	-
2	0.05	0.51	0.52	98.1
3	0.10	0.58	0.57	101.7
4	0.25	0.67	0.72	93.1

Table 8. Determination of Zn in iron minerals and results of recovery tests

Sample	Zn(added)/mg g^{-1}	Zn(found)/mg g^{-1}	Zn(calc.)/mg g^{-1}	Recovery (%)
		Siderite		
1	-	1.33	-	-
2	0.10	1.47	1.43	97.9
3	0.20	1.56	1.53	102.0
4	0.50	1.84	1.83	100.5
		Hematite 1		
1	-	11.87	-	-
2	35.0	45.54	46.87	97.2
3	70.0	83.62	81.87	102.1
4	140.0	151.6	151.87	99.8
		Hematite 2		
1	-	0.128	-	-
2	0.07	0.186	0.198	93.9
3	0.175	0.292	0.303	96.4
4	0.35	0.472	0.478	98.7
		Marcasite		
1	-	43.84	-	-
2	25.0	68.26	68.84	99.2
3	50.0	90.37	93.84	96.3
		Pyrite		
1	-	0.039	-	-
2	0.025	0.059	0.064	92.2
3	0.05	0.084	0.089	94.4
4	0.10	0.130	0.139	93.5

Depending of the content of the elements investigated in the minerals, their determination was performed using FAAS (Zn and Mn) or Zeeman ETAAS (Pb, Co, Cr and Ni). The optimal instrumental parameters used for these determinations are given in Tables 1 and 2.

The determination of these elements was also performed for five iron ore standard reference samples: JSS 813-3, JSS 820-2, JSS 830-3 (Iron and Steel Institute of Japan) and SU-1, SU-1a (Canada Centre for Mineral and Energy Technology). The results of measured and certified values are given in Table 9. As can be seen, the concentration for Pb, Co, Cr, Ni, Mn and Zn using the proposed method are very similar to those provided for the certified samples. A calculation of Student's t-test for our results gives values smaller than the theoretical ones (for 95% confidence level), which means that there are no significant difference between the found and certified values.

Table 9. Determination of Pb, Co, Ni, Cr, Mn and Zn in standard samples

Referent	Element (in %)					
Standard Sample	Pb	Co	Ni	Cr	Mn	Zn
			JSS 813-3			
Certified	-	-	0.007±0.0002	0.002±0.0002	0.054±0.001	-
Found	-	-	0.0067±0.001	0.0019±0.0005	0.049±0.001	-
t-test	-	-	0.52	2.17	1.73	-
			JSS 830-3			
Certified	-	-	0.006±0.0014	0.0168±0.0006	-	0.075±0.002
Found	-	-	0.0059±0.0025	0.0175±0.001	-	0.076±0.0025
t-test	-	-	0.44	1.21		0.69
			JSS 820-2			
Certified	0.0014±0.0003	-	0.0026±0.0006	0.0025±0.0004	0.076±0.001	0.009±0.0006
Found	0.0014±0.001	-	0.0025±0.002	0.0025±0.001	0.074±0.001	0.0089±0.001
t-test	0.0	-	0.34	0.0	3.46	0.17
			SU-1a			
Certified	-	0.041±0.001	1.233±0.008	-	-	-
Found	-	0.040±0.001	1.220±0.010	-	-	-
t-test	-	1.73	2.25	-	-	-
			SU-1			
Certified	-	0.063	-	0.05	0.08	0.0289
Found	-	0.061±0.002	-	-	0.081±0.003	0.0286±0.001
t-test	-	1.73	-	-	0.58	0.52

n = 3

Calibration curves were made using the proposed extraction procedure for standard solutions of the elements investigated. The standard deviations (SD) of the blank sample (n=10) are: 3 ng·g^{-1} for Ni and Cr, 10 ng·g^{-1} for Pb and Co, 0.03 μg·g^{-1} for Zn and 0.08 μg·g^{-1} for Mn. Relative standard deviations range from 0.55% to 2%. The detection limits of the method, calculated as 3 SD of the blank, are 10 ng·g^{-1} for Ni and Cr and 30 ng·g^{-1} for Pb and Co, determined by Zeeman ETAAS, and 0.10 μg·g^{-1} for Zn and 0.25 μg·g^{-1} for Mn, determined by flame AAS. As can be seen, the levels of determination are much higher when the determination is performed by flame AAS than by ETAAS.

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.

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