ANALYSIS OF SULPHIDIC MINERALS
BY ATOMIC ABSORPTION SPECTROMETRY

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The determination of 17 trace and minor elements in sulphidic minerals using atomic absorption spectrometry is described. Samples are decomposed in nitric acid for the determination of Ag, In, Tl, Pb and in a hydrochloric acid–nitric acid mixture for the determination of Zn, Cd, Cu, Mn, Fe, Co, Ni, As, Sb, Bi, Mg, Ca and Cr. The method makes possible to determine Zn, Cu, Cd and Ag concentrations less than 1 p.p.m., Pb, Sb and Bi in the range of p.p.m., and other elements at concentrations higher than 10 p.p.m..

Trace elements in individual sulphidic minerals have a very important role in the investigation of the sulphidic ore deposits formation. From the distribution of these elements it is possible to conclude on the directions of the ore forming solutions uplifts. For these studies it is necessary to analyze separated minerals which often are available in very limited amount. At the same time, a large number of elements has to be quantitatively determined with a high degree of accuracy. Since the main components of the analyzed minerals differ (galenites, sphalerites, chalcopyrites, antimonites, *etc.*), the application of spectroscopic methods where a solid sample is used for analysis (emission spectrometry, X-ray fluorescence spectrometry as well as electron microprobe analysis) meets with the problem of suitable reference samples. Methods which employ solution of the sample do not have such problems and, at the same time, have usually higher accuracy. Atomic absorption spectrometry (AAS) is therefore mainly used in our laboratory for this type of analyses.

In this paper methods for the determination of Ag, Tl, In, Sb, Bi, Pb, Cu, Zn, Cd, As, Fe, Mn, Co, Ni, Mg, Ca and Cr in sulphidic minerals which have been developed and used in our laboratory for several years are reviewed. Although AAS was often adopted[1-3] to determine individual elements in sulphidic materials, our problem was to find conditions under which the maximum number of elements could be determined from one solution without any previous separation.

Since the amount of the available sample is limited, the used analytical method should have a very low limit of determination. This is important because isomineral and heteromineral elements of interest may occur in very low concentrations. In order to make the limit of determination for some elements lower, the application of heated longpath absorption tubes proved to be effective. In this technique the burnt flame gases are led into a tube placed in the optical axis of an absorption spectrometer.

EXPERIMENTAL AND RESULTS

Instrumentation

Perkin-Elmer Model 306 spectrometer with acetylene–air flame burner was used for all determinations. The Perkin-Elmer Model 56 recorder was used to determine low concentrations of elements. A device containing longpath absorption tube was applied to determine such concentrations of elements which are lower than the limits of determination of the used spectrometer. The device consists of a silica tube, $40-45$ cm long and of 10 mm internal diameter, placed in an electric furnace and aligned with the optical axis of the spectrometer. The radiation emitted by a hollow cathode lamp is focused into the tube. The radiation leaving the tube is focused by a spherocylindrical lens on the entry slit of a monochromator. The lens is protected by blowing an air stream which diverts the hot gases passing from the tube up toward an exhaust. The photomultiplier Hamamatsu HTV 136 is attached to the exit slit of the Zeiss SPM-1 monochromator provided with a silica prism. A direct injection burner, type Beckman 4060, for a hydrogen-oxygen flame is used as atomizer. Air of 1 atm pressure is used instead of oxygen. The fuel gas flow rate is adjusted by a gas regulator unit originally belonging to the Optica Milano flame attachment. The angle between the burner and the horizontal optical axis is approximately $30°$.

High voltage power supply for the photomultiplier, the power supply for hollow cathode lamps and a measuring device were built in the Institute of Applied Geophysics, Brno. The hollow cathode lamp power supply is current regulated in the range of $0-50$ mA and produces rectangular pulses of 50 Hz. A lock-in amplifier triggered by the power supply with up to ten times scale expansion is used.

For all elements Perkin-Elmer hollow cathode lamps were used. The Varian-Techtron hydrogen hollow cathodes lamp was applied for background correction in the longpath tubes.

Reagents

For decompositions of the separated minerals hydrochloric and nitric acids of "semiconductor" purity were used. Other used chemicals were analytical reagent grade. Water was redistilled. Stock solutions of elements being determined were mostly prepared by dissolving specpure metals in required amount of an acid. All stock solutions had the concentration of 1 mg/ml. Working reference solutions were prepared by dilution of the stock solutions and contained the identical concentration of acids as the sample solutions (HCl + tartaric acid or HNO_3 + tartaric acid). Four reference solutions were used for each order of magnitude of concentration. Measured concentration ranges are presented in Table I.

Decomposition

Acid decomposition of sulphidic minerals proceeds without difficulties. Two decomposition procedures had to be used. One using nitric acid only, the other with a mixture of nitric and hydrochloric acids. Decomposition with sulphuric acid is not convenient since a strong absorpion background appears when an absorption tube is used for measurements[2].

Nitric acid decomposition. Add 2 ml of 20% tartaric acid solution (10 ml of 20% solution for antimonites) and 10 ml concentrated nitric acid to $0.1-0.3$ g of finely powdered sample. Leave the reaction mixture standing for 12 hours, then complete the decomposition by digestion on a boiling water bath for $2-3$ hours. Just before the end of the decomposition process add 1 ml of 3% $Hg(NO_3)_2$ solution to complex Cl^- ions which may be present in traces[1]. Filter off the

insoluble residue and the precipitated sulphur using filter paper for fine precipitates. Wash the residue in the beaker three times by decantation with water, transfer finally to the filter and there again wash with water. Collect the filtrate into a 50 or 100 ml volumetric flask.

Decomposition by nitric and hydrochloric acid. Decompose $0.1-0.5$ g sample using 10 ml hydrochloric acid. Add H_2O_2 or HNO_3 and evaporate to dryness. Then again add 5 ml HCl and keep warm. After the decomposition has been completed, add 2 ml of 20% tartaric acid. Cool, transfer to a volumetric flask and make the volume up to the mark.

Decomposition of insoluble residue. In separated minerals the insoluble residue is very small, usually $1-2\%$. It is however considerably higher in sulphidic ore concentrates. The fraction of the determined elements in the residue may, nevertheless be, in most cases neglected.

If however the elements in the insoluble residue are to be determined, the filter paper containing the residue is ashed, dissolved in acids and added to the main portion.

Burn the filter paper in a fused-alumina crucible. Moisten the contents of the crucible with 1 ml concentrated nitric acid, add $5-10$ ml 10% HF and evaporate on a hot plate until the residue is still moist but not yet dry. Add 2 ml concentrated nitric acid or hydrochloric acid according to the type of decomposition agent used previously, and keep the covered crucible on a hot plate for another 2 hours. Add the crucible contents to the main portion.

TABLE I

Concentration Ranges of Reference Solutions in µg/ml

Element	Measurement		Recommended decomposition procedure
	absorption tube	Perkin Elmer 306	
Cd	$0.002-0.1$	more than 0.04	a, b
Ag	$0.002-0.2$	0.1	b
Pb	$0.02-0.7$	0.4	b
Sb	$0.04-4$	2	a
Bi	$0.02-2$	1	a
In	$0.1-2$	0.7	b
Tl	$0.1-2$	0.7	b
Zn	—	0.04	a, b
Cu	—	0.1	a, b
Fe	—	0.2	a
Mn	—	0.2	a, b
Ni	—	0.2	a
Co	—	0.2	a
Ca	—	0.1	a
Mg	—	0.02	a
As	—	5	a
Cr	—	0.1	a

Decomposition: a HCl + HNO_3, b HNO_3.

Measurement

The manufacturer's recommended conditions[4] were mostly followed when measuring on the Model 306 spectrometer. Possible deviations are mentioned below. When a longpath absorption tube was used for the measurements, the following procedure was applied: The tube was heated to 1100°C. The burner and the flame were directed so as to make the flame enter the silica tube. The end of the tube is bevelled. The angle between the burner and the optical axis should be chosen so that the flame is reflected from the upper tube wall and flows inside.

The air flow rate is determined by the amount flowing through the burner nozzle at the pressure of 1 atm. The flow of hydrogen is adjusted to maximize the sensitivity for each particular element. This requirement is realized for most elements when the volumes of hydrogen and of air, including air which is entrained from the atmosphere, make approximately a stoichiometric mixture in the tube. If the angle is smaller or the tube diameter larger, more air is entrained from the atmosphere[5] and the necessary amount of hydrogen increases. Some elements, however, require excess hydrogen, the sensitivity for the others may, on the other hand, be reduced by an excess of hydrogen[6,7].

Examples how absorption of some elements depends on the hydrogen flow rate are shown in Figs 1 and 2.

Absorption Background in Longpath Tubes

Due to the long optical path and lower temperature in the tube, the absorption background is higher than for common flames. The background for many elements is however negligible in analysis of separated sulphidic minerals (except pyrites) if oxidation of sulphur to sulphates in the decomposition process is avoided. The background is more pronounced when analysing sulphidic ore concentrates.

A number of compounds in the solution being atomized contribute by their molecular spectra, namely nitrates by molecular bands of NO, and sulphates by SO_2 spectrum. The alkali halides spectra also show characteristic maxima[8]. Higher concentrations of other elements e.g. Mg, Ca,

TABLE II

Analytical Lines and Lines Used to Correct the Absorption Background for the Measurement Using Longpath Tubes

Element	Analytical line Å	Line for correction Å	Band width Å
Ag	3 280·7	Ag 3 215·7	0·6
Cd	2 288·0	Cd 2 306·6	0·3
Pb	2 170·0	Pb 2 203·5	0·4
Pb	2 833·1	Pb 2 802·0	0·4
In	3 039·4	In 2 932·6	0·5
Tl	2 767·9	Tl 2 826·2	0·6
Sb	2 175·8	Sb 2 179·2	0·2
Bi	2 230·6	H_2 lamp	0·3

Al, and Fe produce on the contrary almost uniform absorption of radiation in the entire wavelength range. This absorption increases slightly with decreasing wavelength and it is probably caused by light scatter on non-vapourized particles.

The absorption background is corrected by subtracting the absorbance, measured using an appropriate non-absorbing line at a wavelength close to the analytical line or employing a hydrogen discharge tube, from the absorbance of the measured analytical line. Recommended lines for the background correction are listed in Table II.

Determination of Individual Elements

Silver. The decomposition procedure with nitric acid is used and mercuric nitrate is added after the decomposition has been completed. No background correction is usually needed when using a longpath tube since the background in the region above 3000 Å is negligible.

Bismuth. The decomposition with the nitric acid–hydrochloric acid mixture is convenient. The process should be carried out at laboratory temperature to avoid oxidation to sulphates. If bismuth is determined in antimonites or thioantimonites with high content of antimony, the absorption spectrum of Sb_2 molecules appears in the tube[6]. Such background has to be corrected employing a hydrogen discharge lamp since bismuth possesses no suitable non-absorbing line close to its analytical line and the molecular spectrum of Sb_2 depends on the wavelength considerably.
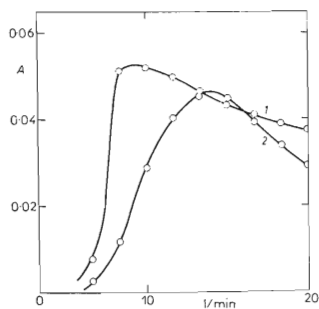

FIG. 1

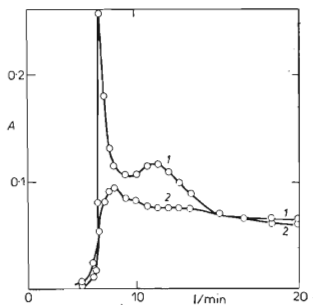Dependence of Bismuth (*1*) and Indium (*2*) Absorbance on the Hydrogen Flow Rate

FIG. 2

Dependence of Copper Absorbance on the Hydrogen Flow Rate

1 0·1 μg/ml Cu in HCl (1 : 20); *2* 0·1 μg/ml Cu in HNO_3 (1 : 20).

Lead. The application of an absorption tube introduces a substantial reduction of the detection limit. The choice is between the Pb 2169·99 Å and Pb 2833·1 Å lines. The former is twice as sensitive than the latter but shows higher noise. Close to both lines are suitable lines for background correction (2203·5 and 2802·0 Å respectively).

Antimony. A very narrow slit width has to be used (maximum band pass 2 Å) since the non-absorbing line Sb 2170·23 Å is partly absorbed by lead[9,10]. With the longpath tube, the slit width used is 0·3 Å.

Cadmium. Cadmium has a very low determination limit hence most samples can be analyzed on a Perkin-Elmer 306 instrument. With an absorption tube the absorption spectrum of SO_2 due to the oxidation of sulphur to sulphates during the decomposition process with nitric acid, interferes strongly.

TABLE III

Comparison of Atomic Absorption Spectrometry Results with Those Obtained by Other Chemical Methods (all data in %)

							Sphalerites						
Pb		Cd		Ag		Cu		Sb		Fe		Mn	
a	b	a	b	a	b	a	b	a	b	a	b	a	b
0·88	0·87	0·84	0·86	0·052	0·051	0·10	0·096	0·052	0·051	1·77	1·75	0·31	0·27
0·26	0·25	1·20	1·30	0·047	0·047	0·030	0·030	0·060	0·063	1·08	1·04	0·003	—
1·10	1·10	1·19	1·27	0·064	0·064	0·075	0·073	0·048	0·050	0·96	0·94	0·089	0·082
0·17	0·16	0·98	1·03	0·025	0·025	0·053	0·050	0·021	—	1·20	1·25	0·038	

							Galenites						
Zn		Cd		Ag		Cu		Sb		Fe		Mn	
a	b	a	b	a	b	a	b	a	b	a	b	a	b
0·59	0·59	0·010	0·010	0·092	0·092	0·012	0·012	0·24	0·22	0·19	0·12	0·22	0·25
0·068	0·070	0·019	0·019	0·065	0·065	0·11	0·097	0·064	0·060	0·21	0·20	0·27	0·26
5·80	5·83	0·097	0·097	0·19	0·20	0·26	0·26	0·27	0·25	3·79	3·82	0·70	0·67
0·12	0·12	0·003	—	0·33	0·34	0·21	0·21	1·10	1·20	1·30	1·28	0·28	0·26
0·12	0·12	0·003	—	0·072	0·073	0·090	0·089	0·44	0·42	0·30	0·30	0·075	0·085

a AAS; *b* other methods.

Copper. The copper content in the analyzed samples is always so high that the determination can be carried out on the Perkin-Elmer 306. Both decomposition methods may be used.

Zinc. Due to the high sensitivity of the zinc line, the measurements are performed mostly on the Perkin-Elmer 306 with the burner perpendicular to the optical axis.

Indium and thallium. Hydrochloric acid strongly reduces the signal of both elements. Nitric acid decomposition is therefore used for measurements with both the acetylene-air flame and the absorption tube. Employing the latter however, the content of Fe and Al in the solution should not exceed 100 µg/ml, otherwise a depressive effect is manifested[11].

Arsenic. The arsenic line is in the far ultraviolet region where the flame absorption is already high. The acetylene-air flame with a three-slot burner is used. A method employing arsenic reduction to arsine which is then introduced into the flame or absorption tube[12], has to be used to determine trace concentrations.

Cobalt and nickel. The determination of both elements using a longpath tube does not show any substantial improvement of the detection limits. When solutions after the nitric acid decomposition are analyzed, the results of Co and Ni may be affected by the depressive effect of iron. Hydrochloric acid is therefore used to decompose the samples. The 2 320 Å line usually recommended as the analytical line for nickel is emitted by the hollow cathode lamp with much lower intensity than the Ni 3 524·5 Å line. The latter line is preferred despite its about three times lower sensitivity, because a much higher scale expansion is possible.

Chromium. The application of longpath tubes does not bring any improvement of the limit of detection. Employing the Perkin-Elmer 306 instrument, a three-slot burner and a strongly reducing flame have to be used to attain maximum sensitivity. Under such conditions the depressive effect of iron becomes evident at concentrations

TABLE IV
Analysis of Canadian Sulphide Ore Standard Sample SU-1 (data in p.p.m.)

Element	Recommended value	Found	Element	Recommended value	Found
Ag	4	3·3	Ni	14 000	15 000
Cd	0·34	0·3	Pb	245	250
Co	510	490	Zn	294	312
Cr	360	367			

higher than 300 µg/ml. It can, however, be eliminated by the addition of ammonium chloride in such amount that the sprayed solution is 4% in NH_4Cl (ref.[9]).

Iron. The hydrochloric acid decomposition is more convenient for iron determinations. If the sample solution contains nitrates, the signal of iron depends on the concentration of the acid and the height of observation in the flame used for actual measurement. The line 3719·9 Å is employed for higher concentrations of iron.

Manganese. Manganese is always determined on the Perkin-Elmer 306. The application of an absorption tube does not reduce the detection limit. The line 4030·8 Å is preferable for the determination of higher manganese contents.

Calcium and magnesium. To eliminate the interference of sulphates and aluminium, a solution being 2% in La^{3+} and 10% in 8-oxyquinoline in dilute (1 : 1) hydrochloric acid is added to the solution of each sample[13]. Identical amounts of a buffer solution (2·5 ml/25 ml) are added to the reference solutions of Ca and Mg.

Accuracy, Precision and Limits of Determination

Relative standard deviation of one determination using the Perkin-Elmer 306 instrument varies between 2 – 5% depending on the particular elements. For determinations employing longpath tubes it can reach 8%. When the absorption background becomes commensurable with the absorption signal of an element, the relative standard deviation may even exceed that value.

For some elements in the higher concentration range accuracy was checked polarographically or spectrophotometrically. Results are presented in Table III. For other elements accuracy was verified by the analysis of an international standard sample of the sulphide ore SU-1 (see[14]) with the results given in Table IV. For several elements (In,Tl) accuracy was checked only by the standard addition method which, of course, is far from providing a full proof.

The described method can be employed to determine as little as 0·1 p.p.m. of Ag, Cd, Zn and Cu, the concentrations of Bi, Pb and Sb in the range of p.p.m. and other elements except arsenic in the concentrations higher than 10 p.p.m.

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