STATE OF ALASKA
Department of Natural Resources
DIVISION OF MINES AND GEOLOGY

LABORATORY REPORT NO. 2

Analysis of Copper, Lead, and Zinc By Atomic Absorption Spectrophotometry

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May 1969

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A B S T R A C T

A study of the operating parameters, limits of detection, anion interference, and precision and accuracy of the analysis of copper, lead, and zinc by atomic absorption spectrophotometry are described. Defining the limit of detection as 3σ above background fluctuation (rather than the more conventional 1% absorption) and defining precision as the coefficient of variation, the following data were obtained using a hot aqua regia leach of 10 or less grams of sample:

ELEMENT	LIMIT OF DETECTION (amount in sample)	COEFFICIENT OF VARIATION	AMOUNT OF ELEMENT IN THE SAMPLE
Cu	1.0 ppm	3.6%	0.25 wt%
Pb	10.0 ppm	4.2%	0.42 wt%
Zn	1.0 ppm	4.2%	0.58 wt%

The above precision values include total variation including sampling. The method described is rapid and well suited for the analyses of ores in a geological laboratory in which metallic and matrix elements vary widely.

The method of standard addition as applied to AAS was also investigated. The method is well adapted to analyses of occasional samples for which standards and a routine method is not available.

I N T R O D U C T I O N

This paper is intended for internal use by the Alaska State Division of Mines and Geology but may be useful outside of the Division to people doing similar work.

The following describes the principles of atomic absorption (Abby, 1967, and Robinson, 1965) and how this method relates to the work of the Division. Atomic absorption spectrophotometry may be viewed as a figurative mirror image of the older and more familiar methods of optical emission spectroscopy and flame emission photometry. In the older methods the various elements of a sample are "excited" by an energy input -- carbon arc in the case of optical emission or a flame in the case of flame photometry. "Excited" means that one or more of the atom's electrons are raised to a higher than normal energy level. As the excited electron returns to a lower energy level, the amount of energy input which initially raised the electron to its excited state is given off at a discrete wave length. That wave length is characteristic for the transition involved and identifies the element. The amount of energy at the characteristic wave length indicates the amount of the element present. During the excitation process only a small portion (estimated less than 1%) of the atoms are actually excited, and the other greater than 99% remain unexcited and are said to be at "ground state".

Ground state atoms are capable of absorbing incident radiation at a discrete wave length known as the resonant wave length. Thus, if the light from an element is passed through a flame into which a solution containing that element is being sprayed, a portion of the incident light will be absorbed by the ground state atoms of the element from the sprayed solution. This process is termed "atomic absorption".

An aqueous solution of the element is not required but is the most common way of presenting the sample. The amount of light absorbed is a measure of the relative number of the atoms of that element present in the sample.

In the AAS (atomic absorption spectroscopy) technique, the incident light is supplied by a hollow cathode lamp which emits the characteristic spectrum of the element in question. The ground state atoms of the elemental vapor from the sample absorb a portion of that incident light. The amount of the incident hollow cathode lamp energy absorbed by the sample's ground state atoms is proportional to the number of ground state atoms present. That principle is used for a quantitative measure. The AAS equipment is designed to present a maximum, and reproducible, number of ground state atoms via a sprayed sample solution to the hollow cathode lamp beam for subsequent absorption of the incident beam.

The resonant (characteristic) energy of the element sought is isolated from that of the other elements of the sample solution by three means: 1) the bulk of the isolation is accomplished by the characteristic energy of the hollow cathode lamp, 2) wave length separation by a grating or a prism monochromator resolves the individual wave lengths, and 3) an interrupted or pulsed power supply minimizes the effect of continuous radiation from the flame by having the photomultiplier detector tuned to the interruption frequency.

AAS, of course, has advantages and disadvantages. Among the advantages are: 1) high sensitivity (ppm to ppb), 2) high spectral resolution, 3) small interelement effects, 4) wide analytical range, and 5) speed of analysis. Disadvantages include: 1) the sample must generally be put into solution, 2) the sample is destroyed, 3) the method is relative and not absolute, 4) reagent purity and sample contamination are problems because of the high sensitivity of the method, and 5) approximately 15 elements are not amenable to the AAS technique.

AAS is well suited to the Division's work of routine analyses of potential ore samples and is excellent for routine geochemical trace element analyses. Its high sensitivity and specificity makes possible some trace element analyses without prior concentration or separation.

E Q U I P M E N T

The atomic absorption spectrophcmeter used by the Division is the standard Techtron AA-4. Acetylene fuel with air support and a standard Techtron AB-41 (10 cm slot) burner with a teflon throated nebulizer have been used to date.

Certain start-up electronic problems were experienced, one with the meter read-out component and one with the lamp power supply. The effects of these problems were minimized because the modular design of the Techtron AA-4 allowed a "loaner" component to be plugged-in while the faulty unit was being repaired by the distributor.

MACHINE OPERATING PARAMETERS

Several operating parameters of the AAS unit were tested to determine the optimum settings for routine analysis. The parameters include: 1) slit width, 2) lamp current, 3) detector and read-out meter gain, 4) burner height, 5) fuel and support settings, and 6) burner angle. The objective is to obtain maximum sensitivity, maximum analytical range, maximum read-out stability, and minimum background.

The slit width, current, and gain relationships were determined by using each individually as a variable and determining the optimum setting. The proper fuel and air settings were determined by finding the settings which yield maximum absorption and maximum flame stability. The optimum burner height was selected as that giving maximum absorption. The burner angle is critical. If it is parallel to the beam it gives maximum absorption. The absorption is decreased at other angles. This feature can be used to increase the analytical range without diluting the sample. The results of these tests are shown in table 1. The settings shown in the table can be used routinely for analyses. The method of extending the analytical range by using a less sensitive absorption line was not tested.

TABLE 1

OPTIMUM MACHINE OPERATING PARAMETERS

ELEMENT	SLIT WIDTH μ	LAMP CURRENT mA	GAIN SETTING	FUEL GAGE SETTING	SUPPORT GAGE SETTING	BURNER HEIGHT SETTING	ANAL. RANGE PPM		ABSORPTION LINE USED, $\mathring{A}$
							PARALLEL* BURNER	VERTICAL* BURNER	
COPPER	50	4	5	2.50	20	5	0.1-10	10-120	3247
LEAD	200	4	10	2.75	22	8	1.0-30	10-100	2171
ZINC	250	6	14	1.75	22	8	0.1-4	3-50	2139

* These values represent the result of rotating the burner 90°. Parallel burner means the length of the burner is parallel to the beam path. Vertical burner means the length of the burner is vertical to the beam path.

SAMPLE AND STANDARD SOLUTION PREPARATION

Samples analyzed by the Division include a wide variety of naturally-occuring rocks and ores. The sample is reduced to minus $\frac{1}{4}$ inch in a jaw crusher and is then further ground in a Braun pulverizer to principally minus 200 mesh. The basic analytical procedure is that developed and described by Tindall (1965, p 339-340 and 1966, p 140).

The weight of a sample to be leached of its Cu, Pb, and Zn can be adjusted according to the estimated metal level in the sample to bring the concentration of metal in the solvent to a convenient analytical level. Sample weights normally range from 1.0g to 0.1g for several percent metal to 10g for the ppm range.

The sample is leached with hot aqua regia, urea is added to destroy the NO_3^- (which would lead to flame instability), the liquor is brought to volume, centrifuged or filtered to remove the solids, and then analyzed by AAS by comparing the sample's absorption to that of standards. Details of the procedure are given in a later section. At least four standards are prepared to form the analytical line.

It has been found that the composition of the liquor has a moderate to strong effect on absorption at a given metal level. This effect was tested by adding precise amounts of Cu, Pb, and Zn to various acids of various strengths and comparing absorptions.

Table 2 shows the absorbance obtained from the three elements in various matrices. The table shows there is a much higher absorption from a pure water matrix than from HCl, HNO_3, or aqua regia, and a much higher absorption from those acids than from H_2SO_4.

A test was made to indicate whether the variation in absorption was related to anion interference or aspiration rate of the analyte. The aspiration rate was tested by aspirating the four different liquids for three minutes. The aspiration rates of the four liquids were found to vary significantly and expressed as a percentage of the amount of water aspirated in unit time, they were:

3:1, HNO_3:H_2O - 78%

3:1, HCl:H_2O - 82%

3:1, Aqua Regia: H_2O - 89%

3:1, H_2SO_4:H_2O - 16%

1:50, H_2SO_4:H_2O -100%

Because the above relationships are similar to the absorbance data of table 2 we believe the variation in absorption is related to the viscosity of the liquid and not to an anion matrix effect. This points out the necessity of having the matrix composition of the standard and sample solutions similar.

The 1:50 H_2SO_4 sample was tested in order to find the significance of sulfate being introduced into the liquor by sulfide samples. The 1:50 H_2SO_4:H_2O is the maximum amount of sulfate introduced from a two gram sample of galena taken to 100ml of liquor. The result being 100% indicates that no significant viscosity, i.e., aspiration rate, effect would be introduced by the sulfide derived from samples themselves.

Also, no effect on absorption was detected by the addition of three times the recommended urea volume.

TABLE 2

AQUEOUS MATRIX EFFECTS

AQUEOUS MATRIX TESTED	ABSORBANCE OBTAINED FROM 40 ppm Pb	ABSORBANCE OBTAINED FROM 20 ppm Cu	ABSORBANCE OBTAINED FROM 10 ppm Zn
3:1, HNO_3:H_2O	0.367	0.347	0.409
3:1, HCl:H_2O	0.393	0.337	0.398
3:1, H_2SO_4:H_2O	0.244	0.292	0.252
3:1, Aqua Regia	0.432	0.398	0.456
H_2O	0.482	0.482	0.523

PRECISION AND ACCURACY

The precision of the analyses was measured by the method of replication on six samples. The precision determined is the total variation and not just the precision related to, say, reading the value from the AAS unit. The precision measurement was obtained by taking six aliquots of powder from one sample and treating each of the six as separate specimens through all the steps of the procedures. Total errors of weighing, pipeting, AAS measurements, etc., are reflected in the stated precision. Further, the precision was determined separately at relatively low, intermediate, and high metal levels.

Table 3 shows the statistical data obtained from these experiments.

TABLE 3

PRECISION OF THE METHOD

ELEMENT	METAL LEVEL % IN SAMPLE	STANDARD DEVIATION	COEFFICIENT OF VARIATION	N, NUMBER OF SAMPLES
Cu	0.016	0.0008	5.1%	6
Cu	0.248	0.009	3.6%	6
Cu	22.4	0.63	2.8%	6
Pb	0.037	0.002	5.4%	6
Pb	0.420	0.018	4.2%	5
Pb	2.16	0.024	1.1%	5
Zn	0.038	0.002	5.4%	6
Zn	0.580	0.018	4.2%	5
Zn	0.950	0.024	1.1%	5

Accuracy is much more difficult to establish. Our accuracy was indicated by some comparisons of our analyses to those made by others. We analyzed a number of samples that were analyzed by one or more other laboratories using various analytical methods. These samples include the Sulfide sample obtained from the Canadian Association for Applied Spectroscopy (Webber, 1968, pp 229-248) and two of the six new silicate reference samples, obtained from the U. S. Geological Survey (Flanagan, 1967, p 289-308), that are supplements to the G-1 and W-1 standards. The values on two other samples were obtained by referee methods from Coast Eldridge, Ltd. of Vancouver, B.C. Table 4 shows our values compared to those of the other laboratories and other methods on the above samples. The correspondence between the results of our analyses and those of other laboratories and of other methods seem to be acceptable.

TABLE 4

COMPARISON OF ANALYTICAL VALUES

SAMPLE	COMMENT	COPPER		LEAD		ZINC	
		OUR RESULTS	OTHER ANALYST	OUR RESULTS	OTHER ANALYST	OUR RESULTS	OTHER ANALYST
34268	Sample from our files	22.4%	22.3%(1)	2.16%	2.06%(1)	1.03%	0.93%(1)
20235	Sample from our files	0.25%	0.22%(1)	0.42%	0.45%(1)	0.58%	0.61%(1)
Sulfide	CAAS Sulfide Spl.	0.76%(1)	0.83%(2)	0.02%	0.02%(2)	0.05%	0.03%(2)
GSP-1	U.S.G.S. silicate sample	43 ppm	50 ppm(3)	46 ppm	60 ppm(3)	116 ppm	600 ppm(3)
BCR-1	U.S.G.S. silicate sample	16 ppm	25 ppm(3)	20 ppm	20 ppm(3)	84 ppm	600 ppm(3)

(1) Referee analysis by Coast Eldridge, Ltd.
(2) Mean of a large number of analyses by various methods (Webber, 1965, pp 229-248). Ranges from which the means were determined are Cu, 0.4 to 1.0%; Pb, 0.020 to 0.030%; Zn, 0.016 to 0.055%.
(3) Mean values obtained by spectrographic analyses from nine different analysts at three different laboratories (Flanagan, 1967, pp 289-308). The ranges are GSP-1, Cu, 34 to 60 ppm; Pb, 50-90 ppm; Zn, not detected.

THE PROCEDURE

AAS OF COPPER, LEAD, AND ZINC

1. Weigh minus 200 mesh sample into a 400 ml beaker. Sample weight may be from 0.1 to more than 10 g. Choose an amount of sample, depending on the estimated concentration of the element in the sample, to allow a convenient analytical range.

2. Slowly add 25 ml of concentrated HCl.

3. Cover and place on a 300° C hot plate.

4. After digesting for 15 minutes add 15 ml of concentrated HNO_3 and 10 more ml of concentrated HCl.

5. Digest for 20 minutes.

6. Add 25 more ml of concentrated HCl and boil for 5 minutes.

7. Add 10 ml of 5% (Wt/Vol) urea in water.

8. Boil five minutes longer.

9. Cool to room temperature and bring to 100 ml in a Nessler color tube or other volumetric vessel with cold H_2O. The solids must be removed. This can be done by centrifuging or by filtering through No. 2 Whatman filter paper.

10. Liquid from the above sample is analyzed with the AAS unit at appropriate machine settings after a 15 minute warm-up period for the machine as follows:

    a. Turn the three "operate" switches to "on", select the desired lamp, lamp current, slit width, burner height, coarse gain, wave length, etc., for the desired analysis as is shown in table 1.

    b. Prepare an aliquot of the sample solution, by dilution if necessary, such that the transmittance is preferably between 80% and 20% while being aspirated into the burner.

    c. Prepare standards (preferably four) of the element in question in an acid matrix to approximately enclose the 20% to 80% transmittance optimum working range. The acid composition of the standards must be similar to that of the sample solution. Zero and balance the machine read-out to give 100% transmittance while aspirating a blank solution of similar acid composition and 0% transmittance with the hollow cathode beam interrupted.

d. Aspirate the standard solutions and plot the absorbance vs. concentration. This plot should yield a straight line. Absorbances obtained by aspirating the sample solutions are then compared to the scribed analytical line.

11. The ppm level in the sample solution can be converted directly to ppm in the solid sample by recalling the weight to volume dilution factor. For example, if 10 g of sample were used and the final sample solution was 100 ml the dilution factor is $\frac{100}{10} = 10$.

If the sample solution is found to contain five ppm of metal, the metal level in the original sample is 5 x 10 = 50 ppm.

STANDARD ADDITION METHOD

The method termed "standard addition" may usually be used: 1) when interference cannot be controlled, 2) when the matrix of the sample differs significantly from that of easily prepared standard solutions, or 3) for occasional samples in which interference and matrix effects are unknown. There are some matrix problems, e.g. molecular absorption (Robinson, 1966, p 8; Billings, 1965, p 357-360; Slavin, 1965, p 360-361) that the standard addition method does not solve. The method is one in which a known amount of the element sought is added directly to an aliquot of the sample solution. The AAS reading from the sample solution is compared to the reading from the solution to which a known amount of the element was added. By "back extrapolation" the amount of element in the original sample solution can be calculated by one of the forms of the basic equation:

$$\frac{x}{x+a} = \frac{A_1}{A_2}$$

where

x = concentration in the unknown sample solution

a = concentration added to the unknown sample solution

A_1 = absorbance on sample solution

A_2 = absorbance on sample solution to which a known amount of the element has been added

It is usually advisable to check the answer by taking two or more aliquots of sample-solution-plus-element at different levels. Equivalent answers, of course, should be obtained. The amount of element to add should be on the order of one-half to twice the amount present in the sample solution. For example, should the sample solution contain an estimated 10 ppm Cu,

then the range of addition should be about 5 to 20 ppm. The standard addition method presupposes that all the points tested lie on a straight portion of the curve of absorbance vs. concentration, and that the extrapolated line passes through zero.

An example of a determination by standard addition follows. The sample is to be analyzed for Zn. One gram of the ground sample is digested in aqua regia according to the procedure previously described, with the final solution brought to 100 ml. Because of high Zn concentration the solution is diluted 1/100. Three 9 ml aliquots of the solution are taken and to one, 1 ml of 0 ppm Zn is added, to the second 1 ml of 10 ppm An is added, and to the third 1 ml of 20 ppm Zn is added. Adding 1 ml of 10 ppm Zn to 9 ml of sample solution makes a total of 10 ml and in effect adds 1 ppm to the entire 10 ml of solution, and similarly with the other solutions so that the three samples are now increased by 0, 1, and 2 ppm Zn. Absorbances read are as follows:

0 ppm added = 0.089
1 ppm added = 0.171
2 ppm added = 0.256

The equation $\frac{x}{x+a} = \frac{A_1}{A_2}$ is rearranged to solve for x as follows:

$$x = \frac{A_1 a}{A_2 - A_1}$$

The values are substituted in the equation giving the following results:

1 ppm added = 1.08 ppm in the original sample solution
2 ppm added = 1.06 ppm in the original sample solution

This is good agreement between the two. Finally, the dilution factor from sample to solution is 10^4 resulting during digestion and dilution, times $\frac{10}{9}$ resulting from the standard addition dilution. Therefore, the answers are: $(1.08)(10^4)(\frac{10}{9})$ = 12,000 ppm and $(1.06)(10^4)(\frac{10}{9})$ = 11,777 ppm, which is 1.20% and 1.18% Zn in the sample.

A number of samples have been analyzed for Cu, Pb, and Zn by both the standard addition method and by comparing to an analytical line. Comparable analytical results were obtained. We have found by replication, analysis by standard addition is usually better than 10% of the value and very high precision and accuracy are possible.

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