

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

LABORATORY REPORT NO. 3

**Geochemical Analytical Procedure For
Copper, Lead, and Zinc by
Atomic Absorption Spectroscopy**

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A B S T R A C T

A procedure for analyzing geochemical samples for copper, lead, and zinc by atomic absorption spectroscopy is described. The precision and accuracy compares rather well with assay type analyses and the results on numerous samples compare well with geochemical analyses from an independent laboratory. The procedure is capable of detecting background levels of the three metals in geochemical samples. The procedure leaches 2 grams of sample in 20 ml of HCl + aqua regia + H₂O in a hot water bath. The analyte is centrifuged and read directly by atomic absorption spectroscopy. Usually no further dilutions are required. Starting from oven-dried, minus 80 mesh material the analysis under optimum conditions requires only about five to ten minutes per sample.

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

A geochemical field investigation requires numerous samples in order to establish a geochemical pattern and significant deviations from the pattern. Because of the large number of samples, an acceptable geochemical analysis requires that it be fast. The best possible precision and accuracy, however, is not required. An additional requirement for geochemical analyses is that the sensitivity be such that the background level, or average level of the metal in non-anomalous sample, is easily detected. This implies that the procedure can detect at least 50 ppm zinc, 20 ppm copper, and 10 ppm lead in the sample (Andrews-Jones, 1968, p 9). Ideally, the procedure should routinely be able to detect the metal at about half the above stated value, although even greater sensitivity is required for some types of samples.

The Division's laboratory has done "ore-type" analyses routinely for Zn, Cu, and Pb by atomic absorption for some time and has accumulated a good deal of experience in the use of the atomic absorption technique. A previous report covers this analysis thoroughly (Anderson and Cho, 1969). The reader may wish to refer to that report for additional details.

E X P E R I M E N T

DIGESTION PROCEDURE

The procedure routinely uses oven-dried (80°C) sample of minus 80 mesh material obtained by sieving through stainless steel. The digestion vessel chosen is a standard glass culture tube* of 20 ml capacity. The procedure uses two grams of sample taken to 20 ml. This system provides

*Can be obtained from Van Waters and Rogers, Cat. No. 60828-241, 16 x 150 mm (20 ml) size, with teflon lined caps.

for: 1) an adequate sample size, 2) convenient analytical range (only rarely would a dilution be required), 3) small enough volume to not be wasteful of reagents, 4) ease of relating metal level in the solution to that in the sample ($20/2 = 10$) and 5) because of the culture tube's small volume and tall form many samples can be digested simultaneously. The tubes are sturdy and fairly easily cleaned.

A test was designed to determine the best acid combination. Three acids (HCl, HNO₃, and aqua regia), and acid combinations, were tested. The design for the test was as follows:

1. add 2 - 3 ml of conc. acid to the empty culture tube
2. add 2.00 g of sample to the acid
3. heat in a near boiling water bath for 15 minutes
4. add a second acid to bring the tube to one-half full
5. add 4 - 6 grains of solid KMnO₄ to help oxidize the sample
6. digest for 45 minutes, then bring to 20 ml volume with deionized H₂O
7. centrifuge

The acid combinations used and the results are shown in table 1. The table shows there is a significant difference depending on the acids used for digestion. Certain combinations are excluded because the vigorous reaction made the digestion impossible. The table also shows a significant difference in metal values depending on the acid combinations. The highest values, and therefore the acid combination adopted, were obtained when using HCl as the starting acid and then adding boiled aqua regia after the initial heating.

The completeness of this geochemical digestion procedure was tested by comparing the values obtained using this method to values obtained with our regular atomic absorption assay procedure. The accuracy of the ore assay procedure has been previously proven. The results are shown in table 2.

TABLE 1

TEST OF VARIOUS ACIDS FOR DIGESTION

| INITIAL ACID 2-3 ml | SECOND ACID TUBE 1/2 FULL | SAMPLE BEHAVIOR DURING DIGESTION | SAMPLE 1 PPM | | | SAMPLE 2 PPM | | | SAMPLE 3 PPM | | |
|------------------------|------------------------------|-------------------------------------|-----------------|----|-----|-----------------|----|----|-----------------|----|-----|
| | | | Cu | Pb | Zn | Cu | Pb | Zn | Cu | Pb | Zn |
| HCl | HCl | boiled over upon heating | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| HCl | Aqua Regia | no problems | 56 | 16 | 127 | 34 | 16 | 89 | 65 | 18 | 103 |
| HCl | HNO ₃ | boiled over upon heating | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| HNO ₃ | HNO ₃ | no problems | 45 | 14 | 93 | 28 | 14 | 72 | 52 | 16 | 88 |
| HNO ₃ | Aqua Regia | no problems | 55 | 16 | 118 | 33 | 14 | 87 | 63 | 18 | 115 |
| HNO ₃ | HCl | boiled over upon heating | -- | -- | -- | -- | -- | -- | -- | -- | -- |

TABLE 2
COMPARISON OF GEOCHEMICAL DIGESTION PROCEDURE
WITH REGULAR ASSAY PROCEDURE

| SAMPLE | <u>COPPER</u> | | <u>LEAD</u> | | <u>ZINC</u> | |
|--------|---------------|---------|-------------|---------|-------------|---------|
| | ASSAY | GEOCHEM | ASSAY | GEOCHEM | ASSAY | GEOCHEM |
| JC-29 | 49 | 46 | 11 | 12 | 99 | 90 |
| JW-93 | 24 | 21 | 14 | 15 | 157 | 148 |
| JC-30 | 56 | 55 | 10 | 10 | 110 | 107 |
| JW-122 | 51 | 48 | 10 | 15 | 132 | 128 |
| GE-11 | 26 | 23 | 10 | 10 | 95 | 90 |

The above table shows that the geochemical digestion procedure may give less than complete digestion; the assay values are slightly higher, but there is not a significant difference. Also, digestion time was investigated. Digestion times of 10 minutes, 20 minutes, 30 minutes, and 45 minutes were used. There was a correlation of completeness of digestion with time. Ten minutes digestion yielded somewhat lower metal values than 20 minutes; there was a possible, very small, difference between the 20 and 30 minutes of digestion; the values stabilized with time of more than 30 minutes. For the routine procedure 40 to 45 minutes is adopted.

TABLE 3
PRECISION TEST OF GEOCHEMICAL ANALYSIS

| SAMPLE | PPM COPPER | PPM LEAD | PPM ZINC |
|---|------------|----------|----------|
| JC 122 A | 32 | 13 | 86 |
| B | 32 | 11 | 91 |
| C | 33 | 11 | 93 |
| D | 32 | 11 | 91 |
| E | 30 | 10 | 90 |
| F | 32 | 9 | 92 |
| JW 120 A | 62 | 16 | 113 |
| B | 62 | 15 | 110 |
| C | 59 | 15 | 105 |
| D | 61 | 16 | 113 |
| E | 62 | 15 | 110 |
| F | 61 | 14 | 110 |
| JC 118 A | 53 | 14 | 110 |
| B | 48 | 13 | 108 |
| C | 53 | 15 | 108 |
| D | 53 | 15 | 113 |
| E | 52 | 14 | 110 |
| F | 53 | 15 | 108 |
| JC 88 A | 31 | 11 | 83 |
| B | 32 | 13 | 85 |
| C | 30 | 11 | 81 |
| D | 30 | 11 | 81 |
| E | 30 | 9 | 83 |
| F | 28 | 11 | 79 |
| Mean coefficient of variation from the four samples | 4% | 10% | 3% |

P R E C I S I O N A N D A C C U R A C Y

A precision test was run on four samples. From each of the four samples six aliquots of sample were randomly chosen from the sample container. Each aliquot was treated as a separate sample. The precision values are then a measure of total analytical error. Table 3 shows the results of the precision test.

An additional test of precision, and a comparison with an independent laboratory, was made on a group of 40 samples. The samples were collected by R. Asher, Division Engineer, during his 1968 field season on the Seward Peninsula and represent a wide variety of sample types. These samples had been previously analyzed by the U. S. Geological Survey Laboratory by atomic absorption spectroscopy, but using a very different digestion procedure. In this test our laboratory analyzed these samples twice -- on different days and by different analysts. The three separate sets of data are therefore completely independent. The results are shown in table 4.

Some comparisons are drawn from table 4. By comparing the arithmetic means of our analyses with those of the U.S.G.S. laboratory systematic biases are detected. This comparison is possible only for Cu and Zn because of the absence of U.S.G.S. values for lead below 20 ppm.

| | <u>ARITHMETIC MEANS</u> | |
|-------------------|-------------------------|-------------|
| | <u>COPPER</u> | <u>ZINC</u> |
| Division Analyses | 25 ppm | 75 ppm |
| U.S.G.S. Analyses | 30 ppm | 70 ppm |

The similarity of the mean values for 40 samples leads to the interpretation that no strong systematic bias exists between the two sets of data.

Another comparison of data is made by calculating the standard deviation of the differences between the three groups of data, i.e., Division Lab. Analyst 1, Division Lab. Analyst 2, and the U.S.G.S. Lab. These results are as follows:

| | <u>STANDARD DEVIATION</u> | | |
|----------------------------|---------------------------|-----------|-----------|
| | <u>Cu</u> | <u>Pb</u> | <u>Zn</u> |
| Div. Lab. 1 vs Div. Lab. 2 | 5 ppm | 3 ppm | 10 ppm |
| Div. Lab. 1 vx U.S.G.S. | 10 ppm | ----- | 15 ppm |

The above data indicates a very close correlation between the data of analyst 1 and analyst 2 of the Division Lab. and also between the labs of the Division and the U. S. Geological Survey

TABLE 4
COMPARISON OF ANALYSES

| SAMPLE | COPPER | | | LEAD | | | ZINC | | |
|--------|------------------|------------------|------|------------------|------------------|------|------------------|------------------|------|
| | DML ₁ | DML ₂ | USGS | DML ₁ | DML ₂ | USGS | DML ₁ | DML ₂ | USGS |
| SP 164 | 18 | 21 | 20 | 10 | 11 | 20 | 65 | 70 | 80 |
| 165 | 26 | -- | 30 | 13 | -- | 20 | 83 | -- | 90 |
| 166 | 30 | -- | 30 | 13 | -- | 20 | 105 | -- | 90 |
| 168 | 22 | 21 | 25 | 11 | 10 | 20 | 72 | 74 | 40 |
| 169 | 24 | 23 | 25 | 11 | 12 | 20 | 65 | 74 | 40 |
| 170 | 19 | 20 | 25 | 10 | 12 | 20 | 68 | 74 | 40 |
| 171 | 16 | 18 | 20 | 10 | 10 | 20 | 58 | 66 | 50 |
| 172 | 24 | 25 | 20 | 10 | 10 | 20 | 88 | 86 | 60 |
| 173 | 15 | 34 | 45 | 9 | 15 | 20 | 51 | 91 | 80 |
| 175 | 15 | 16 | 15 | 9 | 10 | 20 | 51 | 61 | 40 |
| 176 | 22 | 20 | 20 | 11 | 12 | 20 | 73 | 74 | 50 |
| 177 | 31 | 27 | 35 | 13 | 13 | 20 | 87 | 89 | 70 |
| 178 | 25 | 23 | 30 | 11 | 12 | 20 | 74 | 76 | 60 |
| 182 | 43 | 43 | 20 | 17 | 20 | 20 | 98 | 96 | 70 |
| 183 | 24 | -- | 40 | 13 | -- | 20 | 74 | 64 | 70 |
| 184 | 25 | 23 | 30 | 12 | 12 | 20 | 70 | 71 | 70 |
| 187 | 36 | -- | 45 | 16 | -- | 20 | 110 | -- | 100 |
| 188 | 20 | 22 | 40 | 11 | 13 | 20 | 68 | 71 | 60 |
| 189 | 57 | -- | 65 | 35 | -- | 25 | 232 | -- | 200 |
| 190 | 19 | 22 | 30 | 7 | 7 | 20 | 30 | 29 | 40 |
| 191 | 26 | 40 | 60 | 11 | 13 | 20 | 123 | 117 | 130 |
| 192 | 26 | 23 | 35 | 9 | 8 | 20 | 60 | 56 | 60 |
| 194 | 24 | 25 | 30 | 11 | 15 | 20 | 68 | 76 | 60 |
| 195 | 22 | 21 | 25 | 9 | 13 | 20 | 65 | 64 | 50 |
| 196 | 20 | 25 | 20 | 10 | 12 | 20 | 37 | 34 | 40 |
| 197 | 22 | 21 | 30 | 11 | 12 | 20 | 62 | 66 | 50 |
| 198 | 20 | 20 | 35 | 13 | 20 | 20 | 67 | 66 | 60 |
| 199 | 21 | 20 | 25 | 10 | 10 | 20 | 60 | 66 | 50 |
| 200 | 31 | 30 | 40 | 20 | 21 | 20 | 150 | 152 | 140 |
| 201 | 19 | 21 | 30 | 10 | 12 | 20 | 58 | 64 | 70 |
| 202 | 41 | 50 | 60 | 25 | 33 | 20 | 74 | 96 | 80 |
| 203 | 19 | 18 | 25 | 12 | 12 | 20 | 60 | 61 | 60 |
| 204 | 27 | 27 | 40 | 20 | 24 | 20 | 72 | 36 | 80 |
| 205 | 28 | 18 | 20 | 7 | 8 | 20 | 35 | 61 | 50 |
| 206 | 33 | 34 | 45 | 15 | 17 | 20 | 81 | 84 | 80 |
| 207 | 22 | 20 | 25 | 11 | 10 | 20 | 63 | 74 | 50 |
| 208 | 15 | 18 | 20 | 14 | 13 | 20 | 43 | 56 | 40 |
| 209 | 32 | 32 | 35 | 15 | 16 | 20 | 82 | 91 | 70 |
| 211 | 25 | 23 | 25 | 13 | 13 | 20 | 73 | 81 | 50 |
| 212 | 17 | 16 | 20 | 11 | 10 | 20 | 67 | 81 | 70 |

DML₁, Division of Mines Laboratory, P. L. Anderson analyst

DML₂, Division of Mines Laboratory, Namok Cho analyst

USGS, U. S. Geological Survey analyses; all except one sample was below their 20 ppm sensitivity for lead

DATA REPORTING

The Techtron AA-4 unit used in our laboratory is equipped with a device for direct readout of data, eliminating having to form analytical curves from standards each time. Because of this feature and the nature of the needs of geochemical data values should be reported at even five ppm intervals above five ppm, and one ppm intervals below five ppm.

LOWER LIMITS OF ANALYSIS

The procedure described here will routinely yield the following lower limit of analysis for the three elements:

Cu - 1 ppm

Pb - 5 ppm

Zn - 1 ppm

The above limits could be lowered for particular needs, but routine geochemical analyses would not require better sensitivity. The lead analysis uses a 5x scale expansion on the atomic absorption unit. No scale expansion is used for zinc or copper.

SPECIFIC PROCEDURE

Material must be oven-dried and screened to yield minus 80 mesh material for the analysis.

1. To a culture tube add 2 - 3 ml of conc. HCl
2. Weigh and add to the acid 2.00 ± 0.01 g of sample - wash sample into tube with about 2 ml more HCl
3. When all reaction stops, place the tube in a near-boiling water bath (watch for and remove from heat in case of vigorous reaction) for 10 minutes or until reaction stops
4. Add aqua regia* to half fill the tube
5. Add 4 - 6 grains of solid KMnO_4 as an oxidizer
6. When the KMnO_4 is dissolved, cap the tube and shake until all sample is removed from tube bottom
7. Loosen cap and digest in near-boiling water bath for 40 minutes
8. Bring analyte volume to 20 ml with deionized H_2O by filling the tube to a level one-half way up on the neck of the culture tube. When liquid is cool the volume will be very close to 20 ml.

*This aqua regia reagent is formed by one part concentrated HNO_3 , four parts conc. HCl, boiled until nearly clear and diluted to $\frac{1}{2}$ with deionized H_2O .

9. Tighten the culture tube cap and again shake to mix water and remove sample from bottom of the tube
10. Centrifuge at 800-900 RPM for 10 minutes, by use of adaptors 16 samples can be centrifuged simultaneously
11. Read by AAS
12. Report values to the nearest 5 ppm

S P E E D O F A N A L Y S E S

Experience has indicated that starting from oven-dried, minus 80 mesh material, one person can weigh, digest, centrifuge, read by AAS, and record the data for 100 samples in about 8 hours, or approximately five minutes per sample.

REFERENCES

- Andrews-Jones, D. A., The Application of Geochemical Techniques to Mineral Exploration; Mineral Industries Bull., Colorado School of Mines Research Foundation, Inc., Nov. 1968, Vol 11, No 6, p 9.
- Anderson, Paul L. and Namok Cho, Atomic Absorption Analyses for Copper, Lead, and Zinc; Alaska State Division of Mines and Geology, Laboratory Report No. 2, 1969.