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# LABORATORY NOTES NO. 7

# Molybdenum Analysis by Atomic Absorption Spectroscopy

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# MOLYBDENUM ANALYSIS BY ATOMIC ABSORPTION SPECTROSCOPY

## INTRODUCTION

A molybdenum hollow cathode lamp, for analyzing Mo by AAS, has recently been acquired by the Laboratory. Machine operating parameters, sample dissolution method, precision of analysis at two molybdenum levels, and the minimum detection limit have been investigated and are herein reported.

## MACHINE OPERATING PARAMETERS

The preferred machine operating parameters for our Techtron AA-4 units are as follows:

Wave length------------------------------------ 3133A°

Slit width------------------------------------- 50 μ

Hollow cathode lamp current---------------- 7 ma

Air---------------------------------------------- 23 psig

Acetylene-------------------------------------- 4.5

The efficiency of obtaining the molybdenum vapor in the analytical flame is extremely sensitive to flame conditions. The 4.5 acetylene setting shown above is only approximate. Probably the best way to achieve a suitable flame is to adjust the gas flow to yield a 0.30 to 0.35 absorbance while asperating a 100 ppm Mo standard. This will be a very luminous flame.

Because of the sensitivity to flame conditions we have not found it practical to use "Scale Expansion" to increase the limit of detection of the Mo analysis. If fact, a fairly high time constant must be used, three or four setting, to reduce fluctuation to a manageable level.

## SAMPLE DISSOLUTION METHOD

Molybdenite is a difficult mineral to dissolve. The other molybdenum containing minerals dissolve readily in aqua regia. The fastest way we have found to put molybdenite into solution is that suggested by Treadwell and Hall (1942). They treat molybdenite with $HNO_3 + H_2SO_4$, evaporate to fumes of sulfur trioxide, but not to dryness, and then dissolve the residue in aqua regia. The ratio of $HNO_3$ to $H_2SO_4$ = 1.3 - 1.5. The specific steps of the procedures are given in a later section.

## PRECISION OF ANALYSES AND DETECTION LIMIT

A rock sample containing considerable visible molybdenite was broken into about one inch pieces and then two fractions, one with a high molybdenum content and another with a much lower molybdenum content were selected. The samples were crushed to minus 1/4 inch, pulverized to minus 100 mesh, and thoroughly mixed.

Six powder specimens of each of the low and the high molybdenum containing sample were weighed out. One gram specimens were taken of the high Mo sample, and 10 gram specimens were taken of the low Mo sample. The samples were digested by the method described above, diluted to a suitable analytical range and analyzed by AAS.

The analytical results were as follows:

WEIGHT PER CENT MOLYBDENUM

| SAMPLE | High Mo | | Low Mo | |
|---|---|---|---|---|
| | Reading 1 | Reading 2 | Reading 1 | Reading 2 |
| 1 | 23.5 | 23.0 | 0.595 | 0.595 |
| 2 | 23.5 | 22.5 | 0.585 | 0.585 |
| 3 | 24.0 | 23.5 | 0.585 | 0.585 |
| 4 | 24.5 | 24.0 | 0.565 | 0.555 |
| 5 | 24.0 | 24.5 | 0.610 | 0.610 |
| 6 | 25.0 | 25.0 | 0.630 | 0.610 |
| Average | 23.7 | 23.7 | 0.596 | 0.590 |
| Grand Average | 23.7 | | 0.593 | |

The standard deviation and coefficient of variation was calculated for each sample series. Also, the standard deviation and coefficient of variation was calculated for the two separate readings on the low molybdenum sample. This allows some estimate of the source of variation, ie, between separate specimens compared to separate machine readings. The total standard deviation represents the variation due to the aggregate affects of sampling, weighing, pipeting, and machine variation. The results of the calculations follow:

| SAMPLE* | AVERAGE | STANDARD DEV., TOTAL | COEFFICIENT OF VARIATION, MACHINE | COEFFICIENT OF VARIATION, TOTAL |
|---|---|---|---|---|
| High Mo | 23.7% | 0.90 | not determined | 3.8% |
| Low Mo | 0.593% | 0.0153 | 0.6% | 2.6% |

* Six samples in each group

An estimate of the limit of detection is made by defining the limit of detection as 2 percent absorbance. This was found to be equivalent to about 1 ppm in the analyte. Considering sample to analyte dilution of ten (10-gram sample taken to 100 ml) the detection limit in the sample would be 10 ppm.

## DISCUSSION

The method seems to be reliable and fast. The precision is surprisingly good considering the necessary character of the flame for molybdenum. The sensitivity is poorer than was hoped, particularly since scale expansion cannot be used. Ten ppm Mo in the sample is somewhat above geochemical background for Mo. According to Hawkes and Webb (1962) background geochemical levels for Mo range as low as 0.2 ppm. Possibly an extraction - concentration procedure would allow the geochemical determination of molybdenum by AAS.