

This document was produced  
by scanning the original publication.

Ce document est le produit d'une  
numérisation par balayage  
de la publication originale.

CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA

MINES BRANCH INVESTIGATION REPORT

IR 71-35

May 6, 1971

THE DETERMINATION OF BISMUTH,  
IRON, MOLYBDENUM, AND SULPHUR IN  
A PROPOSED STANDARD MOLYBDENITE  
ORE, REF. No. PR - 1

by

A. W. Ashbrook and D. Barkley

EXTRACTION METALLURGY DIVISION

Mines Branch Investigation Report IR 71-35

THE DETERMINATION OF BISMUTH,  
IRON, MOLYBDENUM, AND SULPHUR IN  
A PROPOSED STANDARD MOLYBDENITE  
ORE, REF. No. PR - 1

by

A. W. Ashbrook\* and D. Barkley\*\*

====

SUMMARY

Analyses for bismuth, iron, molybdenum, and sulphur obtained by this laboratory as part of a collaborative scheme on the certification of standards of Canadian ores are reported. The methods used and the precision of the results obtained are also described.

---

\*Assistant Head and \*\*Scientific Officer, Chemical Analysis Section, Extraction Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

## INTRODUCTION

The Mineral Sciences Division of the Mines Branch, Department of Energy, Mines and Resources, has undertaken a programme to prepare a number of standard samples of typical Canadian ores. The first of these, a molybdenite ore obtained from Preissac Molybdenite Mines Ltd. (Western Quebec), was submitted by Mr. G. H. Faye of the Mineral Sciences Division<sup>(1)</sup>.

The sample, prepared by the Mineral Sciences Division, had been ground to minus 200 mesh, blended, and checked for homogeneity by instrumental and chemical tests. Minerals, present in the sample, and their approximate abundance had been determined by X-ray diffraction, microscope, and by electron-probe. The following approximate composition was provided:

quartz	90%
K-feldspar	5%
muscovite	3%
molybdenite	1%
pyrite	0.5%
fluorite	0.25%
Fe-Mn garnet	0.1%
chlorite	0.1%

Other minerals found to be present in amounts less than 0.1% were bismuthinite, native bismuth, chalcopyrite, galena, hematite,

ilmenite, magnetite, pyrrhotite, rutile, sphalerite, and nickel-bearing mineral. An approximate chemical composition was also provided, and is given below -

Mo	0.6%
Bi	0.1
Fe	1.3
S	0.8
Cu, Ni, Pb, Zn	<0.05 (each)

Two 8-oz bottles of the sample were received and analyses carried out on each sample. These were designated PR-1, Case 1, Box 2 (EMQ 2806) and PR-1; Case 9, Box 3. (EMQ 2807)

#### EXPERIMENTAL

Descriptions of the methods employed in the analyses are outlined for each element.

##### Bismuth

Dissolution: Two methods of dissolution were tried, a multi-acid treatment and fusion with potassium pyrosulphate. Acid dissolution involved nitric acid - hydrochloric acid (aqua regia) attack and evaporation to dryness. This was followed by hydrochloric acid - hydrobromic acid and evaporation to dryness. Finally nitric acid and perchloric acid were used with evaporation to strong fumes. The residue was heated with 1M sulphuric acid and filtered. The filtrate was used for analysis.

The other dissolution procedure consisted of fusion of about 1 g of sample with about 10 g potassium pyrosulphate in a platinum crucible. The cooled melt was leached with 1M nitric acid and filtered. Bismuth was determined as the yellow/orange-colored iodobismuthite ion (2) produced by the addition of an excess of potassium iodide to an aliquot of the sample solution. Oxidising agents, for example ferric iron, were reduced with ascorbic acid and sodium sulphite. Absorbance of the solution was measured at 450 nm.

In order to determine whether impurities such as iron and tin were interfering in this direct procedure, aliquots of the sample solution were treated with an ammoniacal solution of EDTA and sodium cyanide, and the pH adjusted to about 9 with ammonium hydroxide. A solution of sodium diethyldithiocarbamate (DDTC) was then added and the Bi- DDTC complex extracted with carbon tetrachloride. The carbon tetrachloride was evaporated in the presence of dilute sulphuric acid, perchloric acid added and the solution heated to strong fumes to remove organic material. The solution remaining (~ 0.5 ml) was diluted with 5 ml of 5M sulphuric acid and transferred to a 50-ml volumetric flask. Bismuth was determined as described above.

Results by this procedure agreed well with those obtained, without extraction, after pyrosulphate fusion.

Consistent results could not be obtained on sample solutions prepared by multi-acid treatment. All results were low (0.01 - 0.5% Bi) and varied with the size of aliquot taken for bismuth determination.

#### Iron and Molybdenum

Iron and molybdenum were determined on aliquots of the same solution. Sample dissolution was effected by heating with a mixture of nitric and hydrochloric acids (aqua regia). After the addition of perchloric acid, heating to strong fumes and dilution with water, the residue was filtered and washed with water. The residue was then ignited in a platinum dish, treated with hydrofluoric and sulphuric acids and fumed to dryness. The remaining residue was fused with potassium pyrosulphate, the melt dissolved in water, the solution added to the main filtrate, and diluted to volume in a volumetric flask.

#### Determination of Iron

Iron was determined colorimetrically on an aliquot of the sample solution by the formation of the ferrous ortho-phenanthroline complex, at pH 3.8, after reduction with hydroxylamine<sup>(2)</sup>. Absorbance measurements were made at 510 nm.

Results obtained by multi-acid treatment only were generally low by about 0.3% (absolute).

### Determination of Molybdenum<sup>(3)</sup>.

Molybdenum was determined colorimetrically as the orange/red-colored molybdenum thiocyanate produced in hydrochloric acid solution by reduction of molybdenum (VI) to molybdenum (V) with stannous chloride in the presence of ammonium thiocyanate. The molybdenum thiocyanate was extracted into a n-butyl acetate and the absorbance of the extract measured at 470 nm.

### Sulphur

Sulphur was determined by a combustion technique<sup>(4)</sup>. The sample was ignited in an induction furnace, in an oxygen atmosphere, by which the sulphur was converted to sulphur dioxide. This was oxidised to sulphuric acid by bubbling through a solution of hydrogen peroxide (10%), and the acid so produced was titrated continuously with a standard sodium hydroxide solution using mixed methylene blue and methyl red as indicator. The procedure was checked using BCS Sample No. 301 (Lincolnshire Iron Ore) having a total sulphur content of 0.470%. The furnace used was a LECO Model No. 523, and the sulphur titrator was a modified LECO Model No. 400-I.

### RESULTS

Results of the analyses of the two samples received are given in Table 1. Assuming the two samples to be identical,

TABLE 1

Analyses Obtained on Molybenite Ore Standard PR-1

Sample	Bismuth %	Iron %	Molybdenum %	Sulphur %
PR-1	0.11 <sub>7</sub>	1.23 <sub>2</sub>	0.58 <sub>9</sub>	0.79 <sub>3</sub>
Case 1, Box 2	0.11 <sub>7</sub>	1.22 <sub>9</sub>	0.58 <sub>3</sub>	
	0.11 <sub>3</sub>	1.22 <sub>3</sub>	0.58 <sub>9</sub>	0.79 <sub>7</sub>
	0.11 <sub>5</sub>	1.22 <sub>7</sub>	0.58 <sub>7</sub>	
EMQ 2806	0.11 <sub>9</sub>	1.21 <sub>2</sub>	0.58 <sub>6</sub>	0.80 <sub>5</sub>
	0.11 <sub>8</sub>	1.21 <sub>2</sub>	0.57 <sub>1</sub>	
	0.11 <sub>5</sub>	1.21 <sub>5</sub>	0.58 <sub>9</sub>	0.79 <sub>2</sub>
	0.11 <sub>5</sub>	1.21 <sub>4</sub>	0.58 <sub>1</sub>	
	0.11 <sub>8</sub>	1.21 <sub>5</sub>	0.58 <sub>2</sub>	0.78 <sub>9</sub>
	0.11 <sub>7</sub>	1.21 <sub>3</sub>	0.57 <sub>2</sub>	
Average = 0.11 <sub>6</sub> 1.21 <sub>9</sub> 0.58 <sub>3</sub> 0.79 <sub>5</sub>				
PR-1	0.11 <sub>9</sub>	1.23 <sub>1</sub>	0.58 <sub>9</sub>	0.79 <sub>3</sub>
Case 9, Box 3	0.11 <sub>7</sub>	1.23 <sub>3</sub>	0.58 <sub>3</sub>	
	0.11 <sub>9</sub>	1.23 <sub>2</sub>	0.58 <sub>6</sub>	0.80 <sub>6</sub>
	0.11 <sub>7</sub>	1.23 <sub>4</sub>	0.57 <sub>3</sub>	
EMQ 2807	0.12 <sub>3</sub>	1.21 <sub>5</sub>	0.59 <sub>4</sub>	0.80 <sub>4</sub>
	0.11 <sub>9</sub>	1.21 <sub>4</sub>	0.58 <sub>3</sub>	
	0.12 <sub>1</sub>	1.22 <sub>7</sub>	0.59 <sub>3</sub>	0.80 <sub>1</sub>
	0.11 <sub>9</sub>	1.22 <sub>1</sub>	0.59 <sub>9</sub>	
	0.11 <sub>9</sub>	1.22 <sub>1</sub>	0.59 <sub>0</sub>	0.79 <sub>3</sub>
	0.11 <sub>4</sub>	1.21 <sub>8</sub>	0.59 <sub>7</sub>	
Average = 0.11 <sub>8</sub> 1.22 <sub>5</sub> 0.58 <sub>9</sub> 0.79 <sub>9</sub>				

Loss on drying at 110°C for 24 hours: EMQ 2806 : 0.085%  
 EMQ 2807 : 0.087%

Brackets indicate two aliquots from one weighed portion.

Analyses are reported on an "as-received" basis.

relative standard deviations and the relative 95% confidence limits for the average of 10 duplicate determinations, were:

Bi;	$\pm 1.70\%$ ;	95% CL = $\pm 1.15\%$
Fe;	$\pm 0.63\%$ ;	$\pm 0.45\%$
Mo;	$\pm 0.97\%$ ;	$\pm 0.69\%$
S ;	$\pm 0.78\%$ ;	$\pm 0.56\%$

There was no significant difference between samples at the 5% level of significance.

#### REFERENCES

1. Petruk, W., Mineral Sciences Division, Mines Branch, Internal Report MS 71-27 (1971).
2. Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd Edn., Interscience, New York, N.Y., 1959. p 332.
3. Fortune, W. B., and Mellon, M. G., Ind. Eng. Chem., Anal. Ed., 10, 60 (1938).
4. Rodden, C. J., "Analytical Chemistry of the Manhattan Project" 1st Edn., McGraw-Hill, New York, N.Y., 1950 p 454.
5. Ashbrook, A. W., "The Volumetric Determination of Sulphur in High-Sulphur-Containing Materials," Eldorado Nuclear Ltd., Report A62-3 (1962).