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INTRODUCTION

The determination of molybdenum by atomic absorption has received considerable attention. Several investigators have evaluated the effects of interfering elements and the process of overcoming the effects by the addition of aluminum or ammonium salts (1, 2, 3, 4, 5, 6). Solvent extraction systems used ammonium pyrrolidine dithiocarbamate (APDC) (7, 8), 8-hydroxyquinoline (7, 9, 10, 11), dithiol (11), 2-octanol (12), n-amyl acetate (13). These systems are quite efficient although the extractions require close control of pH. Iron, an interfering element that seriously depresses molybdenum absorption, is often co-extracted into the organic phase.

Liquid ion exchangers, (i.e., quaternary ammonium halides) have been used with advantage in many analytical applications. The selected ion exchanger should not be soluble in water, but soluble in an organic solvent. The halide ion is exchanged with the anion of interest in the aqueous layer and thus concentration of the anion is achieved, while eliminating interfering elements, by extraction into an organic solvent. Accurate control of pH is not necessary to achieve complete extraction.

This paper will describe a method for the determination of molybdenum in geological materials.

It is known that molybdenum as molybdate or phosphomolybdate ion can be extracted using the liquid ion exchanger, Aliquat 336 (methyl tricapryl ammonium chloride, available from General Mills, Inc., Kankakee, Ill.). Aliquat 336 has been used for analytical separation of gold (14), tungsten (15), and actinide-lanthanide elements (16, 17).

PROCEDURE

Mix 0.2 g of finely ground geological sample with 1 g of lithium metaborate and fuse for 15 minutes in a graphite

crucible (18). Cool the melt and drop the globule with forceps into a 50-ml test tube containing 10 ml of a mixture of 10% phosphoric acid and 2% H₂O₂. Phosphoric acid converts the molybdenum to phosphomolybdate. Hydrogen peroxide is added to ensure conversion of all of the molybdenum to the hexavalent state. Any lower valence molybdenum is not extractable with this system. (With this system no interference due to iron occurs. Addition of 0.2 g of Fe to the aqueous phase did not cause any suppression of molybdenum signal.) Place the test tubes on a magnetic stirrer hot plate and continue stirring and heating until the sample is all in solution. Cool the test tube and add 10 ml of MIBK containing 3% Aliquat 336. When greater concentration ratios are desired, 5 ml MIBK can be used. Shake for one minute and measure the molybdenum content of the organic layer by atomic absorption after the phases separate.

Standards: Fuse 0.3751 g of MoO₃ with 2 g of lithium metaborate in a platinum crucible. Dissolve the fusion in dilute phosphoric acid (as described above) and make up to 250 ml. The resulting solution will be a 1000 µg/ml aqueous molybdenum standard. This is further diluted and extracted into MIBK containing Aliquat 336 to give 0.5, 1, 2.5, 5, 7.5 and 10 µg/ml standards.

Analysis of Geological Samples for Molybdenum

Five samples containing molybdenum were analyzed by the proposed method, using a Perkin-Elmer Model 303 atomic absorption spectrophotometer with a nitrous oxide-acetylene flame. The samples were also sent to three commercial laboratories. The results are compared in Table I. The precision obtained for the first four samples is quite good. The poor precision for sample No. L566 is apparently due to sampling errors (particle sparsity effect). The agreement between results obtained by the proposed method and by the commercial laboratories is quite good.

TABLE I
 Analysis of Geological Materials for Molybdenum

Sample No	Atomic Absorption, ppm	Average	Coeff. of Variation (%)	Commercial Laboratories					
				A ^a				B ^b	C ^b
				1	2	3	Av.		
L292	355, 355, 355, 333, 368, 368, 388, 353, 353, 367	360	3.8	530	340	380	417	380	338
L302	190, 195, 212, 201, 210, 208, 202, 202, 203, 203	203	2.9	175	258	202	215	200	182
L346	183, 168, 160, 158, 182, 155, 155, 175, 160, 161	166	5.4	152	142	150	148	160	141
L357	100, 100, 100, 105, 95, 100, 105, 105, 100, 105	102	2.2	106	96	96	99	83	87
L566	32, 25, 24, 29, 25, 29, 35, 25, 33, 36	29	14.7	20	68	23	37	14	25

a. Colorimetric analysis, 1 and 2 — coarse samples, 3 — reground samples.
 b. Acid digestion followed by atomic absorption analysis.

Table II shows the results of an analysis of U.S.G.S. rock standards for molybdenum by this method compared with the reported average value (19). The analytical procedure is the same as described earlier except that only 5 ml of MIBK was used. A scale expansion of 10x and a noise suppression setting of 2 were used. Considering the low level of molybdenum the agreement is quite good. The sensitivity obtained was 0.1 ppm/1% absorption.

TABLE II
Molybdenum in Standard Rock Samples

U.S.G.S. Rock Standards	ppm Mo	
	A.A.	Average Flanagan (19)
BCR-1	5.0	3.9
PCC-1	4.1	5.5
DTS-1	4.2	6.6
AGU-1	6.5	3.7

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