DETERMINATION OF MOLYBDENUM IN ROCKS BY ATOMIC ABSORPTION SPECTROMETRY WITH ELECTROTHERMAL ATOMIZATION AFTER ITS SEPARATION WITH α-BENZOINOXIME

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A method has been worked out for a sensitive and accurate determination of molybdenum in rocks in contents of the order of 10^{-1} g/t. The sample is decomposed with acids and molybdenum is separated from practically all other elements by extraction with α-benzoinoxime from solution of 1·5M hydrochloric acid and 0·13M tartaric acid into chloroform, and determined in the extract by AAS with electrothermal atomization. The quantitativeness of the extraction has been examined and the optimum conditions for the determination in a graphite furnace have been established. The effects of chloroform and of the graphite atomizer on the signal of molybdenum have been investigated, and the accuracy of the method has been tested on GXR geochemical standards.

Molybdenum in geological samples can be conveniently determined[1–3] by flame AAS. The matrix elements, however, interfere even when using the C_2H_2–N_2O flame. A reduction in the interference can be achieved by adding phosphoric or sulphosalicylic acid or Al(III) salts. A direct determination of Mo by electrothermal atomization is difficult even if a background correction is accomplished[4–8], and in geology this approach has only been applied to the determination of Mo in sea water[7]. Salts of alkali metal and alkaline earth (Ca) elements in higher concentrations, and also mineral acids except nitric acid[8–10], bring about a depression of the signal.

In view of the complexity of the matrix, with a high concentration of salts, arising from the decomposition of geological samples, molybdenum should be separated prior to its determination. Extraction separation is preferred with regard to the fact that in this manner the element is not only isolated but also preconcentrated. For the purposes of flame AAS, Mo has been separated in complexes with rhodanide, 8-hydroxyquinoline, dithiocarbamates, and dithiol[11], and also by using liquid ion exchangers[12,13]. The most selective extracting agent for Mo(VI) is apparently α-benzoinoxime, by means of which a separation of molybdenum from a 10^5-fold excess of uni- to trivalent cations has been achieved in mineral acid solutions; only Cr(VI), W(VI), V(V), Nb(V), Zr(IV), and Pd(II) are co-extracted[14–21]. In the presence of tartaric acid and a Fe(II) salt, only Mo and, in part, W are extracted into chloroform[18,20]. Separation with α-benzoinoxime has been employed for the flame AAS determination of molybdenum[17,18], the sample, however, had to be treated before to measurement (evaporation of $CHCl_3$ and decomposition of the chelate).

In the determination of Mo in sea water by electrothermal AAS, the element has been separated with a selective reagent, *viz.* ammonium pyrrolidinedithiocarboxylate[10,22], and with *p*-aminobenzylcellulose[23] (Chitosan). In the analysis of metal impurities in silver, extraction with O-isopropyl-N-methylthiocarbamate has been applied[24].

EXPERIMENTAL

Solutions and Apparatus

The equipment was as follows: A Varian AA-875 ABQ atomic absorption spectrometer fitted with a hollow cathode lamp heated by a 10 mA current. The measurements were carried out on a resonance line at 313·3 nm with the spectral interval of 0·5 nm. A Varian CRA 90 graphite atomizer; the following temperature program was applied unless stated otherwise: drying at 60°C (20 s), decomposition at 700°C (15 s), atomization at 2 400°C (3 s); the atomization ramp rate was 800°C/s. A Varian graphite tube pyrolytically coated. Sheath gas: argon, flow rate 5 l/min. Injection: 5 μl of chloroform solution using a micropipettor of Scientific Glass Engineering (Ringwood, Australia) or a Varian ASD-53 automatic dispenser. The absorbance was evaluated, based on the peak heights, on a Philips PM 8131 recorder.

The standard solution of molybdenum containing 1 mg Mo/ml was prepared by dissolving 1·5000 g of MoO_3 in 50 ml of a 2% NaOH solution and diluting to 1 litre. The working solution containing 1 μg Mo/ml was prepared by dilution. Fresh 0·2% solution of α-benzoinoxime in chloroform and 10% solution of Mohr's salt were prepared prior to the extraction. All the chemicals used were of reagent grade purity (Lachema, Brno).

Procedure

The sample ground to $d_p < 0·06$ mm (0·5—2 g) is decomposed with hot concentrated HNO_3 (20 ml) and concentrated HF (60 ml) in a PTFE beaker, and the solution is evaporated. To the residue are added hydrochloric acid 1 : 1 (20 ml) and bromine water (10 ml), and the whole is heated to remove excess bromine. The solution obtained is filtered over a dense filter into a 100 ml volumetric flask, and the filter is washed with small portions of hot water so that the volume of filtrate does not exceed 60 ml. To the filtrate is added 20% tartaric acid (10 ml), and the solution is neutralized with 10M-NaOH and acidified with concentrated HCl (15 ml); a 10% solution of Mohr's salt is then added (5 ml), and the solution is diluted to volume. A 10 ml aliquot is extracted in a syringe with 5 ml of solution of α-benzoinoxime in chloroform, the organic phase separated is evaporated, and the residue is dissolved in exactly 2 ml of chloroform.

The reference solutions are prepared from the working Mo solutions.

RESULTS AND DISCUSSION

Rock samples can become contaminated with molybdenum during the crushing and homogenization procedure. Therefore, the effect of crushing in seven crushers containing 0·002—0·03% Mo in the steel of the crushing faces was tested on five kinds of rocks, *viz.* graywacke, granodiorite, magmatic gneiss, limestone, and quartz. A comparison of the analyses for samples treated in the crushers and those handled in an agate equipment revealed contamination by molybdenum in the range of 0·1 to 0·7 g/t. Also, the stainless steel sieves, containing 1·6% Mo, were found to contribute to the contamination, therefore, bronze sieves are to be used for controlling the grain size. Molybdenite containing lubricants (Molyka) must by eliminated from the grinding procedure.

The extraction separation of the Mo chelate with α-benzoinoxime (HL) into chloroform has been studied extensively[14–18]; the data reported differ somewhat as to the concentration of the reagent and the number of repetitions of the extraction. We examined the extractability of Mo from a model matrix of Na, Ca, Mg, Cu, Cd, Pb, Ni, Fe, Al, Ti, As, Sb, and Cr with a 0·2% solution of HL in $CHCl_3$. A 100 ml volume of the aqueous phase was extracted with three 10 ml portions of the reagent solution for 2 min. The dependence of the Mo signal on the number of extractions is shown in Fig. 1 for various Mo concentrations. Two 10 ml portions of the HL solution were found sufficient for a virtually complete extraction. This classical extraction procedure was applied to the analysis of rock samples so that the two extraction fractions were filtered over a dry filter paper, the paper was washed with 10 ml of chloroform, and the volume of the organic phase was reduced to about 5 ml by evaporation, transferred into a 10 ml volumetric flask, and diluted to the mark.

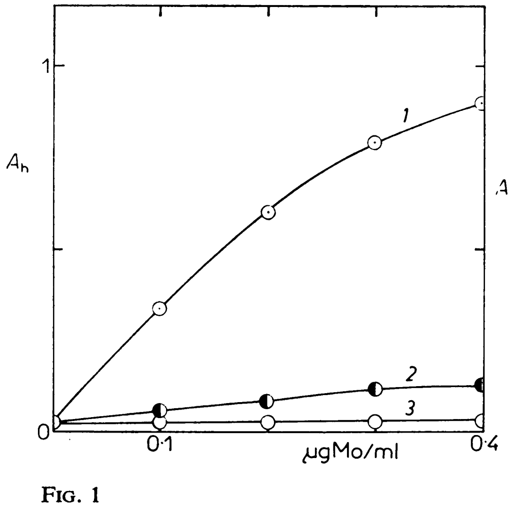

FIG. 1

Dependence of absorbance on the concentration of Mo in three successive 10 ml extracts; $w_{HL} = 0{\cdot}2\%$ in chloroform, $V_{org}/V_{aq} = 0{\cdot}1$. Extract: *1* 1st, *2* 2nd, *3* 3rd

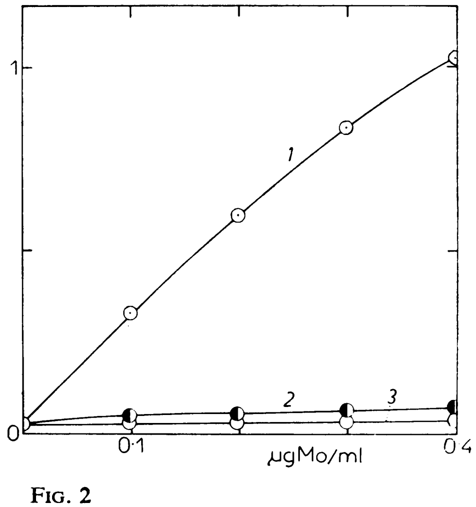

FIG. 2

Dependence of absorbance on the concentration of Mo in three successive 5 ml extracts obtained by extraction in a syringe. Chloroform, $w_{HL} = 0{\cdot}2\%$, $V_{org}/V_{aq} = 0{\cdot}5$. Extract: *1* 1st, *2* 2nd, *3* 3rd

More convenient is extraction in 20 ml polypropylene syringes[25]; the separation of the organic phase by means of a capillary is perfect, no chloroform remains on the walls, and the organic phase need not be freed from water. A 95% extraction is achieved by a single extraction with 5 ml of the 0·2% HL solution in $CHCl_3$ (Fig. 2). After evaporation, the sample can be dissolved in a volume of chloroform at will. the smallest volume used by us, in which the excess reagent still dissolved, was 2 ml. The MoO_2L_2 chelate is extracted into chloroform over a wide Mo concentration region, but at concentrations in excess of 10 μg Mo/ml the chelate is sparingly soluble in chloroform. For the preparation of the reference solutions, the organic phase is conveniently transferred into 10 ml volumetric flasks, where the solutions can be stored in cold and darkness for several weeks.

Molybdenum is among elements that are difficult to atomize (m.p. 2 610°C). Low evaporable Mo_2C and MoC carbides (m.p. 2 960 and 2 965°C, respectively) are formed in the graphite atomizer, whereupon an incomplete evaporation of the metal and a partial atomization of the carbide (memory effect) take place. This effect can be suppressed to an extent by using an atomizer with a pyrolytic coating, but as the atomizer is repeatedly used, the pyrolytic coating deteriorates, and consequently the absorbance signal decreases gradually and the atomizer memory gets more pronounced. The absorbance is to be evaluated from the peak height, and if the limit of detection is approached, from the difference between the signals of the sample and of the empty atomizer.

The optimum atomization temperature, as read from the atomization curve (Fig. 3), is 2 400°C. Here the memory effect is also lowest. The furnace need not be heated-out after each atomization for removing the nonevaporable carbide; for the CRA there is a hazard of degradation. The curve of the thermal decomposition of the MoO_2L_2 chelate in $CHCl_3$ differs from the corresponding curve for the aqueous solution. The depressive effect of the chlorinated solvent[26-28] is marked in an aged graphite tube at temperatures up to 500°C. Part of the chloroform remains bonded in the graphite and brings about a gas phase depression during the atomization. The time courses of the AAS signals for the aqueous and the chloroform solutions show that the activation energy of evaporation is the same; the atomization of Mo is little affected by the halogenated solvent, and the atomizer memory also is not increased appreciably. Thermogravimetric measurements of the MoO_2L_2 chelate give evidence[29] that the ultimate product of pyrolysis is MoO_3, which is stable over the temperature region of 555–780°C. The temperature of 700°C was chosen by us as the most suitable for the thermal decomposition, although no signal decrease was observed up to 1 700°C.

During the heat treatment of sample in the presence of chloroform, interferences are conceivable from volatile chlorides, *viz.* $MoCl_5$ (b.p. 268°C) and $MoCl_4$ (b.p. 322°C), which can decompose thermally to react with MoO_3 giving rise to oxide-

-chlorides[30] such as MoO_2Cl_2 (b.p. 268°C). In the measurements of the absorption of the deuterium lamp radiation at 280 and 226 nm (absorption bands of $MoCl_5$ and MoO_2Cl_2, respectively), no signals were obtained from an aqueous solution containing 1 mg Mo/ml and 5 μl $CHCl_3$. When the MoO_2L_2 chelate was delivered, only a nonselective absorption by the products of its decomposition was observed. A portion of the chloroform solution of MoO_2L_2 was evaporated to dryness and the residue was dissolved in the same volume of methyl isobutyl ketone. The signals of Mo in the two organic solvents were lower than that of the aqueous solution, which is probably associated with the wetting of the surface in the atomizer (Fig. 4).

The magnitude of the Mo signal is affected markedly by the ageing of the graphite furnace. The signal decreases with increasing number of atomizations in such a manner that the plot has the shape of a reverted "S" (Fig. 5). Pyrolytically coated tubes, Varian A 7521 – UT6 and A-9220-UT-6 (threaded) and Ringsdorff Werke RWO 278/PyC and RWO 278/1 PyC (threaded), and CRA tubes of Elektrokarbon, Topolčany coated with layers of pyrolytic graphite 9–12 μm and 19 μm (prototype) thick were tested. The Varian A-7521-UT-6 atomizer exhibits a rapid drop of sensitivity

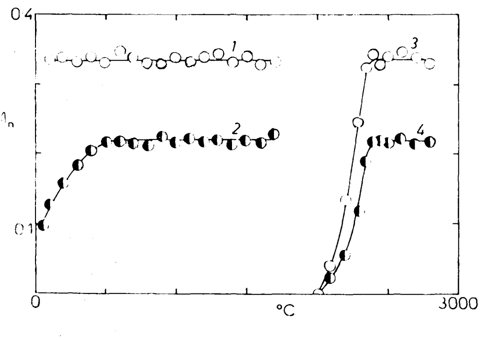

Fig. 3

Thermal decomposition and Mo atomization curves. Solutions: 0·1 μg Mo/ml, aqueous solution of 0·1% HNO_3 (*1*, *3*), or 0·1 μg Mo/ml, MoO_2L_2 chelate in $CHCl_3$ (*2*, *4*). Drying at 60°C (20 s), variable decomposition (15 s), atomization at 2 400°C (3 s) (curves *2*, *4*); drying at 60°C (20 s), decomposition at 700°C (15 s), variable atomization (3 s) (curves *1*, *2*)

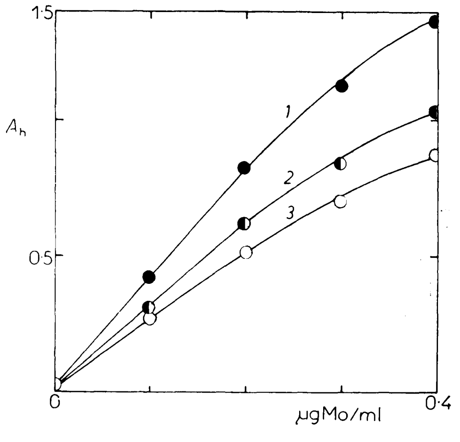

Fig. 4

Calibration curve of Mo in a graphite atomizer. Temperature program: drying at 60–110°C (20 s), decomposition at 700°C (15 s), atomization at 2 400°C (3 s). Atomizer: RWO 278/1 PyC. *1* aqueous solution of 0·1% HNO_3, *2* MoO_2L_2 chelate in $CHCl_3$, *3* MoO_2L_2 chelate in MIBK between the 10th and 30th firings, where the signal decreases nearly to a half of the initial value; then the sensitivity remains constant (200 firings tested). With the Ringsdorff atomizers the signal drop is less dramatic. The threaded tubes provide higher signals than the plain ones. The tubes of Elektrokarbon display a lower initial sensitivity and the EKT 219/3-770 type with a pyrolytic coating thickness of 9 – 12μm has a higher memory, but the SE 233 type with a layer of pyrolytic graphite 19 μm

TABLE I

Content of molybdenum in GXR standards (Geochemical Exploration Samples, U.S. Department of the Interior, Geological Survey Denver, Colorado)

Method	Content of Mo, g/t, in the standard				
	GXR 1	GXR 2	GXR 3	GXR 5	GXR 6
AAS – ETA	11·6	0·6	1·8	34·5	1·7
OES – ICP	12·0	0·7	2·0	34·5	1·6
Recommended value[33]	9·9	1·5	$<6^a$	30	1·7

[a] Content of W 10 800 g/t.

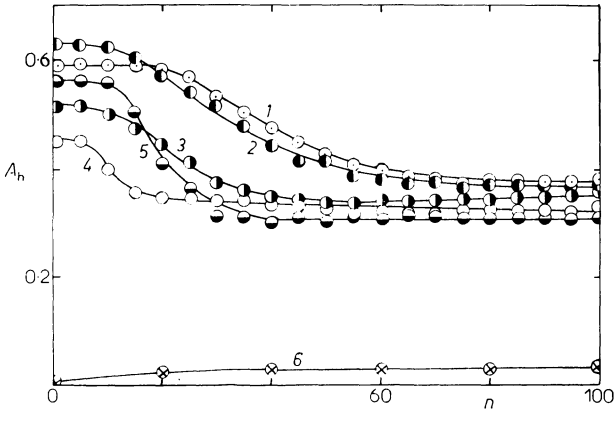

FIG. 5

Dependence of the signal of Mo on the number of atomizations (n). MoO_2L_2 chelate in $CHCl_3$, $\varrho_{Mo} = 0{\cdot}2$ μg/ml, $w_{HL} = 0{\cdot}4\%$, 5 μl injected with a Varian ASD 53 automatic proportioner. Atomizer: 1 RWO 278/1 PyC, 2 Varian A-9220-UT-6, 3 RWO 278/PyC, 4 EKT SE 233 19 μm PG, 5 Varian A-7521-UT-6 PG 3859-I-A; 6 residual signal after a 3 s atomization, virtually identical for atomizers 1–5 thick gives a relatively constant signal. At the time that the furnace sensitivity drops, the measurement cannot be evaluated based on a single calibration plot; the samples have to be measured in combination with the reference solutions. Attention must be paid to an accurate drawing-up of the 5 μl volumes of chloroform; injection of the liquid through a side opening proved well. No background correction is necessary.

Tungsten can be partly co-extracted into chloroform during the extraction of molybdenum with α-benzoinoxime and exert a depressive effect on the signal of molybdenum; this has been explained[31,32] in terms of the formation of stable compounds in the Mo–W–C system suppressing the atomization of Mo. The effect of WO_2L_2 chelate on MoO_2L_2 was therefore examined by us. The chelates were dissolved in chloroform and mixed in proportions as high as 2·0 μg W/ml per 0·1 μg Mo/ml (the tungsten chelate is sparingly soluble in chloroform). In fact, no depressive effect of tungsten was observed.

The accuracy of the results was evaluated based in a comparison with the data of the emission of Mo measured on a Philips PV 8210 spectrometer with an ICP PV 8490 source using the Mo II line at 218·6 nm (Table I).

The detection limit, calculated as three times the standard deviation for 20 blank determinations, was 0·0036 ng Mo. The characteristic concentration giving rise to a 1% absorption was 0·0126 ng Mo. The standard deviation for the extraction and ETA, calculated from 12 determinations of granite (Černá Hora) with an average content of 0·65 ppm Mo, was 0·03 ppm.

REFERENCES

1. Butler L. R. P., Matthews P. M.: Anal. Chim. Acta *36*, 319 (1966).
2. Delanghter B.: At. Absorption Newslett. *4*, 273 (1965).
3. Chan Y. K., Lum Shue Chan K.: Anal. Chim. Acta *48*, 205 (1969).
4. Donega H. M., Burgess T. E.: Anal. Chem. *42*, 1521 (1970).
5. Schweizer V. B.: At. Absorption Newslett, *14*, 137 (1975).
6. Sneddon J., Ottaway J. M., Rowston W. B.: Analyst *103*, (London) 776 (1978).
7. Nakahara T., Chakrabarti C. L.: Anal. Chim. Acta *104*, 99 (1979).
8. Neuman D. R., Munshower F. F.: Anal. Chim. Acta *123*, 325 (1981).
9. Studnicki M.: Anal. Chim. Acta *51*, 1336 (1979).
10. Barbooti M. M., Jasim F.: Talanta *28*, 359 (1981).
11. Kim G. H., Owens C. M., Smythe L. E.: Talanta *21*, 445 (1974).
12. Kim C. H., Alexander P. W., Smythe L. E.: Talanta *22*, 739 (1975).
13. Kim C. H., Owens C. M., Smythe L. E.: Talanta *23*, 229 (1976).
14. Jeffery P. G.: Analyst (London) *81*, 104 (1956).
15. Goldstein G., Manning D. L., Menis O.: Anal. Chem. *30*, 539 (1958).
16. Wish L.: Anal. Chem. *34*, 625 (1962).
17. Hutchinson D.: Analyst (London) *97*, 118 (1972).
18. Donaldson E. M.: Talanta *27*, 78 (1980).
19. Thompson B. A., La Fleur P. D.: Anal. Chem. *41*, 852 (1969).
20. Holnes H. J., Stone K. G.: Talanta *4*, 250 (1960).

21. Pfeifer V., Hecht F.: Z. Anal. Chem. *177*, 175 (1960).
22. Moniem H., Bovenkerk R., Kringe K. P., Rath D.: Fresenius' Z. Anal. Chem. *300*, 363 (1980).
23. Muzzarelli R. A. A., Rochetti R.: Anal. Chim. Acta *64*, 371 (1973).
24. Staseva E. A., Popova N. M., Yudelevich G., Vanifatova N. G., Zolotov Y. A.: Fresenius'
23. Muzzarelli R. A. A., Rochetti R.: Anal. Chim. Acta *64*, 371 (1973).
Z. Anal. Chem. *300*, 28 (1980).
25. Morrison G., Freiser H.: *Extrakční metody v analytické chemii*, p. 85. Published by SNTL, Prague 1962.
26. Gomišček S., Lengar Z., Černetič J., Hudnik V.: Anal. Chim. Acta *73*, 97 (1974).
27. Volland G., Kölblin G., Tschöpel P., Tölg G.: Fresenius', Z. Anal. Chem. *284*, 1 (1977).
28. Karwowska R., Bulska E., Hulanicki A.: Talanta *27*, 397 (1980).
29. Dupuis T., Duval C.: Anal. Chim. Acta *4*, 173 (1950).
30. Opalovskii A. A., Tychinskaya I. I., Kuznetsova Z. M., Samolev P. P.: *Galogenidy Molibdena.* Nauka, Novosibirsk 1972.
31. Rubeška I., Korečková J.: Chem. Listy *73*, 1026 (1979).
32. Throop G. J., Rohl P., Rudy E.: High Temp. Press. *10*, 553 (1978).
33. Gladney E. S., Perrin D. R., Owens J. W., Knob D.: Anal. Chem. *51*, 1557 (1979).

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