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Determination of Small Amounts of Molybdenum in Niobium and Tantalum by Atomic-absorption Spectroscopy in a Nitrous Oxide - Acetylene Flame

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Between 0·006 and 0·06 per cent. of molybdenum can be determined in niobium or tantalum by extracting molybdenum(VI) 8-hydroxyquinolinate from a medium containing fluoride and EDTA as masking agents into butanol at pH 4·5, and atomic-absorption spectroscopy of the extract in a nitrous oxide - acetylene flame at 3132 Å without recourse to scale expansion. The most suitable conditions for the determination have been established, and a study of the effect of other cations and anions is presented. Vanadium(V) and chromium(VI) interfere when present in 100-fold excesses, but their interference can be eliminated by the addition of potassium sulphite to the solution before extraction.

THE determination of refractory elements in matrices which also form refractory oxides can be accomplished by atomic-absorption spectroscopy, if good sensitivity can be obtained by the provision of flame conditions suitable for the production of a large population of ground-state atoms of the element to be determined. Elwell and Gidley[1] have shown that use of the organic solvent effect, after separation by solvent extraction of the element to be determined, can produce increased sensitivity, and such a separation stage can make the procedure virtually specific. Our studies have been concerned with the determination of trace elements in niobium and tantalum by atomic-absorption spectroscopy.[2] Several workers[3,4] have reported the determination of molybdenum by atomic-absorption spectroscopy in an air - acetylene flame. They had to use a fuel-rich luminous flame to provide suitable reducing conditions to obtain a sufficiently large population of atoms and thus achieve a good sensitivity for molybdenum. However, the use of strongly luminous flames is physically unpleasant, and the photomultiplier receives high background radiation that can cause fatigue of the photo-responsive surfaces of the cathode, even although the continuum radiation is not amplified.

The use of a non-luminous nitrous oxide - acetylene flame[5] to obtain a population of ground-state molybdenum atoms suitable for atomic-absorption spectroscopy is reported here. Molybdenum is separated from niobium and tantalum by extraction of molybdenum(VI) 8-hydroxyquinolinate from fluoride medium at pH 4·5 into butanol. The butanol extract, to which butylamine is added to maintain molybdenum(VI) 8-hydroxyquinolinate in solution, is then aspirated into the nitrous oxide - acetylene flame for absorbance measurement at 3132 Å.

EXPERIMENTAL

APPARATUS—

The equipment used was the Unicam SP900A flame spectrophotometer, with a Unicam molybdenum hollow-cathode lamp. The instrument conditions used were: lamp current, 15 mA; wavelength, 3132 Å; and slit width, 0·02 mm. The burner for atomic-absorption measurements in air - acetylene supplied with the SP900A was replaced by a brass burner of similar dimensions for the nitrous oxide - acetylene flame. This burner, which has a slit 2 inches long and 0·015 inch wide, has already been described.[6] A nitrous oxide pressure of 15 p.s.i. was used, and sufficient acetylene to produce the maximum height of red "feather," above the primary reaction zone, without luminosity elsewhere in the flame. Measurements of absorption arising from molybdenum were made in the red "feather" zone of the flame. The flame was first ignited on a fuel-rich air - acetylene mixture (air pressure 15 p.s.i.) and the air was then gradually replaced by nitrous oxide (via two rotameters and a T-piece arrangement) until the air was completely shut off.

REAGENTS—

Molybdenum solution, 10^{-2} M—Dissolve 1·766 g of analytical-reagent grade ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 1 litre of distilled water in a calibrated flask. Dilute this stock solution (960 μg of molybdenum per ml) to 10^{-3} M as required.

Tantalum solution—Dissolve 10 g of tantalum powder (obtained from Murex Ltd., Rainham, Essex) in 30 ml of 40 per cent. hydrofluoric acid and 3 ml of nitric acid (sp.gr. 1·42). Dilute the solution to about 500 ml, adjust to pH 4·5 with 4 M ammonia solution, and dilute to 1 litre to produce a 10,000-p.p.m. tantalum solution.

Niobium solution—Dissolve 10 g of niobium metal (obtained from Murex Ltd., Rainham, Essex) in 30 ml of 40 per cent. hydrofluoric acid and 12 ml of nitric acid (sp.gr. 1·42). Dilute the solution to 500 ml, adjust to pH 4·5 with 4 M ammonia solution, and dilute to 1 litre to produce a 10,000-p.p.m. stock solution.

Buffered 8-hydroxyquinoline reagent—Prepare a 1 per cent. solution of 8-hydroxyquinoline in pH 4·5 sodium acetate - acetic acid buffer. (100 g of hydrated sodium acetate and 150 ml of glacial acetic acid diluted to 1 litre.) All other reagents used should be of analytical-reagent grade.

PROCEDURE—

Calibration graph for molybdenum in niobium (or tantalum)—Transfer 1 to 10-ml aliquots of 10^{-3} M molybdenum solution to a series of 500-ml separating funnels. Add to each solution 150 ml of the 10,000-p.p.m. niobium (or tantalum) solution, 10 ml of a 0·1 M EDTA solution and 50 ml of the 1 per cent. 8-hydroxyquinoline reagent - buffer solution. Add 20 ml of butanol to each funnel and shake the flasks for 1½ minutes. Allow the solutions to stand for 15 minutes for complete phase separation to occur, and discard the aqueous layer. Add 5 ml of butylamine to each organic phase. Spray the clear organic phases directly into the nitrous oxide - acetylene flame and measure the absorbance at 3132 Å against a butanol solvent blank. The use of a butanol - butylamine mixture is not necessary, because the latter does not affect the absorbance readings.

Preparation of samples—Dissolve 1·5 g of niobium or tantalum in 4·5 ml of 40 per cent. hydrofluoric acid and add nitric acid (sp.gr. 1·42), 0·5 ml for tantalum and 1·75 ml for niobium. Dilute to about 75 ml, adjust the pH to 4·5 with 4 M ammonia solution, and then dilute the solution to 150 ml with distilled water.

RESULTS AND DISCUSSION

A calibration graph for molybdenum in aqueous solution can be obtained in the range 20 to 200 p.p.m. of molybdenum (absorbance 0·06 to 0·39). This sensitivity is insufficient to permit the direct determination of small amounts (less than 0·1 per cent.) of molybdenum in niobium and tantalum to be made, and it is not possible to achieve these concentrations by dissolving a large sample of either metal in a small volume of solution suitable for atomic-absorption measurements. The preliminary separation of the molybdenum by extraction of molybdenum(VI) 8-hydroxyquinolinate into butanol was, therefore, adopted to provide a concentration of the molybdenum and to take advantage of the higher spraying efficiency of the organic solvent.

EXTRACTION PROCEDURE—

Chloroform has been the most extensively studied solvent for the extraction of molybdenum(VI) 8-hydroxyquinolinate from aqueous solution, and according to Starý,[7] quantitative extraction may be obtained with 0·01 M 8-hydroxyquinoline in chloroform in the pH range 1 to 5·5. Chloroform, however, is unsuitable as a solvent for atomic-absorption spectroscopy in a nitrous oxide - acetylene flame because during its aspiration it is not possible to make the flame sufficiently non-luminous to obtain the characteristic red "feather" of the nitrous oxide - acetylene flame. The noise-to-signal ratio is, therefore, high, and the flame resembles a luminous air - acetylene flame in its properties. For this reason we preferred to use butanol. Atomic-absorption measurements on both the aqueous and butanol phases over a range of pH values revealed that molybdenum(VI) 8-hydroxyquinolinate was extracted quantitatively into butanol from an aqueous solution, 0·016 M with respect to 8-hydroxyquinoline, in the range of pH 2 to 5. The extraction of molybdenum at pH 4·5 was not inhibited when the solution was also 0·08 M or 0·04 M with respect to niobium or tantalum, respectively, and 0·6 M and 5×10^{-3} M in fluoride and EDTA, respectively. The presence of this concentration of EDTA permits the quantitative extraction of molybdenum from aqueous solutions containing large amounts of other ions (*e.g.*, copper, nickel and cobalt) that would otherwise interfere by consumption of the 8-hydroxyquinoline reagent. The concentration of fluoride present in the aqueous medium (0·06 M) is sufficient to retain the niobium and tantalum in solution as their fluoride complexes, and also to supplement the EDTA as a masking agent for foreign ions that would otherwise form their 8-hydroxyquinolinates and deplete the 8-hydroxyquinoline available for formation and extraction of molybdenum(VI) 8-hydroxyquinolinate.

ORGANIC SOLVENT EFFECT—

Butanol, sp. gr. 0·8, is appreciably soluble in water (7·9 g per 100 ml at 20° C). An aqueous phase volume of 220 ml at room temperature should, therefore, dissolve about 20 ml of butanol. The high ionic strength of the aqueous phase containing the niobium or tantalum, fluoride and EDTA, however, suppresses the miscibility so that when 20 ml of butanol is equilibrated with the aqueous phase (220 ml) at room temperature, 4 ml of butanol solvent phase remain after separation. Over [the normal range of laboratory temperatures encountered, this phase volume is quite reproducible. The use of 25 or 30 ml of butanol for the extraction provides only one-half or one-third of the absorbance on measurement. This decrease in sensitivity is caused by the effective 2 or 3-fold increase in the butanol phase volume to 10 and 15 ml, respectively, after extraction.

After extraction of the molybdenum(VI) 8-hydroxyquinolinate into butanol at pH 4·5, the solution was allowed to stand for 15 minutes for complete phase separation to occur, and the aqueous layer was then rejected. The remaining butanol phase was cloudy and contained an appreciable amount of solid material, whereas the blank solutions that contained no molybdenum did not. This indicated that the precipitate was molybdenum(VI) 8-hydroxyquinolinate, and it was identified as such by filtering off, ashing and testing the dissolved residue (molybdenum trioxide) with 2-amino-4-chlorobenzenethiol hydrochloride.[8] The precipitate, caused by the limited solubility of hydrated molybdenum 8-hydroxyquinolinate in butanol, gave rise to poor reproducibility and lack of sensitivity when the butanol phase was directly aspirated for atomic-absorption measurements. A 5-ml portion of butylamine was, therefore, added to the butanol phase after separation. The amine displaces the water molecules coordinated to the molybdenum in the chelate and thus promotes solubility of the complex in butanol. This addition causes an improvement in reproducibility of the absorbance measurements, and effects an enhancement in sensitivity, even after allowing for the dilution effect, arising from the high atomiser efficiency of butylamine.

CALIBRATION GRAPHS AND SENSITIVITY—

The calibration graphs obtained by the recommended procedure are linear in the range 96 to 960 μg of molybdenum, and correspond to the added 64 to 640 p.p.m. (0·006 to 0·064 per cent.) of molybdenum in the niobium or tantalum sample taken, which is equivalent to 1·5 g of either metal. The absorbance values corresponding to these concentrations are 0·07 and 0·735, respectively, for molybdenum in niobium, and 0·067 and 0·710, respectively, for molybdenum in tantalum. Both calibration graphs pass through the origin, and reveal that the niobium and tantalum metal available to us contained no detectable amount of molybdenum. Although the lowest amount of molybdenum determined in this study corresponded to 0·006 per cent. of niobium or tantalum, the adoption of scale expansion of the 80 to 100 per cent. transmission range, in a manner similar to that described by David,[3] would readily allow the determination of molybdenum to be effected down to 0·001 per cent.

PRECISION AND ACCURACY—

To evaluate the precision of the method, nine simulated niobium-sample solutions containing the equivalent of 320 p.p.m. (0·032 per cent.) of molybdenum in niobium were analysed by the recommended procedure. The standard deviation obtained was 2·9 per cent. of the average absorbance. The analysis of nine similar tantalum-sample solutions gave a standard deviation of 2 per cent. of the average absorbance.

A measure of the accuracy of the method was obtained by the determination of molybdenum in synthetic niobium and tantalum solutions treated as unknown samples. The results of these analyses are shown in Table I.

TABLE I

DETERMINATION OF MOLYBDENUM IN NIOBIUM AND TANTALUM SOLUTIONS

Molybdenum present, per cent. × 10^{-2}	Molybdenum found, per cent. × 10^{-2}	Metal present
3·2	3·0	tantalum
4·5	4·7	tantalum
5·1	5·1	tantalum
1·9	1·9	tantalum
3·2	3·4	niobium
4·5	4·7	niobium
1·9	1·9	niobium
3·5	3·6	niobium
2·3	2·3	niobium

INTERFERENCES—

The effect of foreign ions on the determination was investigated by observing their influence on the absorbance produced in the determination of 0·032 per cent. (480 μg) of molybdenum in niobium and tantalum. An ion was considered not to interfere, for the purpose of this study, when less than 5 per cent. error in absorbance was produced. In the presence of 10 ml of 0·1 M EDTA and from 0·6 M fluoride solution, the presence of a 100-fold excess by weight of the following ions produced no interference: Al, Ca, Co(II), Cu(II), Fe(III), Hg(II), K, Mg, Mn(II), Na, NH_4, Ni, Pb, Sn(IV), Ti(IV), Th, W(VI), Zn, Zr, acetate, chloride, fluoride and sulphate. The presence of a 100-fold excess of vanadium(V) and of chromium(VI) caused low results, but this was eliminated by the addition of 2 g of potassium sulphite to the aqueous solution before addition of the 8-hydroxyquinoline and extraction, and by boiling to promote formation of the chromium(III) - EDTA complex. It is well known that molybdenum(VI) is not reduced under these conditions, and we have checked this by observing no difference in molybdenum absorbance for synthetic mixtures of molybdenum with niobium and tantalum in the presence and absence of potassium sulphite. The vanadium(V) is easily reduced to the vanadium(IV) - EDTA complex, and the reduction of chromium(VI) to chromium(III) is similarly assisted by the EDTA present.

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