Interference by copper(II) in determination of molybdenum(VI) using toluene-3,4-dithiol

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Interference by Copper(II) in Determination
of Molybdenum(VI) Using Toluene-3,4-Dithiol

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MICROGRAM QUANTITIES of molybdenum(VI) are commonly determined after reaction with toluene-3,4-dithiol (H_2D) to form the green trisdithiolate (MoD_3) (*1*). This compound is insoluble in water but readily dissolves in organic solvents (*2-8*). In benzene, the molar absorptivity has been reported as 2.86×10^4 at 665 nm (*9*) and 2.3×10^4 at 682 nm (*10*). Interference by the following elements has been reported: iron, arsenic, antimony, tungsten, and selenium (*8*); platinum and rhenium (*9*); tin, bismuth, titanium, vanadium, zinconium, thorium, and uranium (*10*); and copper (*5, 8-14*).

Data available on copper interference is fragmentary and conflicting. Piper and Beckwith (*5*) found an enhancement due to copper and recommended a preliminary separation involving selective extraction of the dithizone complex of Cu. Bingley (*4, 12*) found a negative interference which was suppressed by the addition of thiourea. Stanton and Hardwick (*8*) also reported negative interference and noted that the order of addition of reagents was critical; increased tolerance to copper was obtained in the presence of iodide and at high acidity. However, using similar conditions, Clark and Axley (*9*) preferred the reverse order of addition of reagents and found no interference effect at a copper-to-molybdenum ratio of 100/1. In $3M$ H_2SO_4, Ssekaalo (*13*) found no copper interference.

The following experiment was undertaken to examine the effect of copper, in the absence of masking agents, on the determination of molybdenum using dithiol. Individual and combined effects caused by variations in the concentration of copper, molybdenum, and hydrochloric acid are separated. The ratios of copper to molybdenum cover the range most often encounted during analysis of biological and mineral materials.

EXPERIMENTAL

Reagents. Solutions of high purity copper (0, 10, 20, 50, 100, and 1000 μg ml^{-1}) and molybdenum (0, 2.5, 5, and 10

Table I. Copper Precipitated (μg) in the Presence of Excess Dithiol from HCl of Various Concentrations

Added copper, μg	Molarity of hydrochloric acid						
	0.5	1	2	3	5	7	10
10	9.5	9.3	7.7	6.5	0.3	0.1	<0.05
20	19.9	19.3	17.3	13.3	2.3	...	0.9
50	49.8	48.6	48.0	41.1	16.5	12.7	...
100	98.9	98.4	96.2	90.5	51.2	43.2	15.0
1000	998	997	994	971	823	713	150

μg ml^{-1}) were prepared in dilute HCl. Concentrated HCl with less than 0.001 μg of Cu and Mo ml^{-1} was diluted with distilled water to 0.5, 1, 2, 3, 5, 7, and 10M.

Procedure. All 168 unique combinations of copper (1.00 ml), molybdenum (1.00 ml), and hydrochloric acid (20.0 ml) reagents were prepared, in duplicate, in 18-mm bore borosilicate tubes. Two milliliters of dithiol (0.2% w/v) (*13*) were mixed with each solution which was then allowed to stand, with occasional shaking, at 20 ± 5 °C, for one hour. Reagent grade isoamyl acetate (5.00 ml) was added and the tube stoppered and shaken vigorously for one minute; the liquid phases were separated by centrifuging.

Molybdenum was spectrophotometrically determined (*14*) in the isoamyl acetate extract and copper was measured in the filtered aqueous phase using atomic absorption spectrophotometry (*15, 16*). The precipitate was digested to dryness with HNO_3 and $HClO_4$ and the residue dissolved in dilute HCl. The resulting solution was analyzed for molybdenum and copper.

RESULTS AND DISCUSSION

Direct Effects of Changing HCl Concentration. In the absence of copper(II), increasing the concentration of HCl from 0.5-10M caused an apparent 24% increase in the quantity of MoD_3 extracted. However, this increase resulted from a corresponding decrease in the volume of isoamyl acetate after equilibration over aqueous phases of increasing HCl concentration. The volume decrease was approximately proportional to the increase in HCl concentration over the 0.5-10M range. All results calculated from the quantity of extracted MoD_3 have been corrected for the change in solvent volume. Based on the present data, previously reported effects (*10, 13*) of increased acid concentration (>1N) on the formation, color intensity, and recovery of MoD_3, are attributed to acid-dependent solvent miscibility.

Increased acid concentration also depressed formation of the insoluble copper dithiol complex. Below $3M$ HCl, copper was almost quantitatively precipitated, but above $5M$ HCl, precipitation was sharply reduced (Table I). The quantity of molybdenum present had no measurable effect on the extent of copper precipitation.

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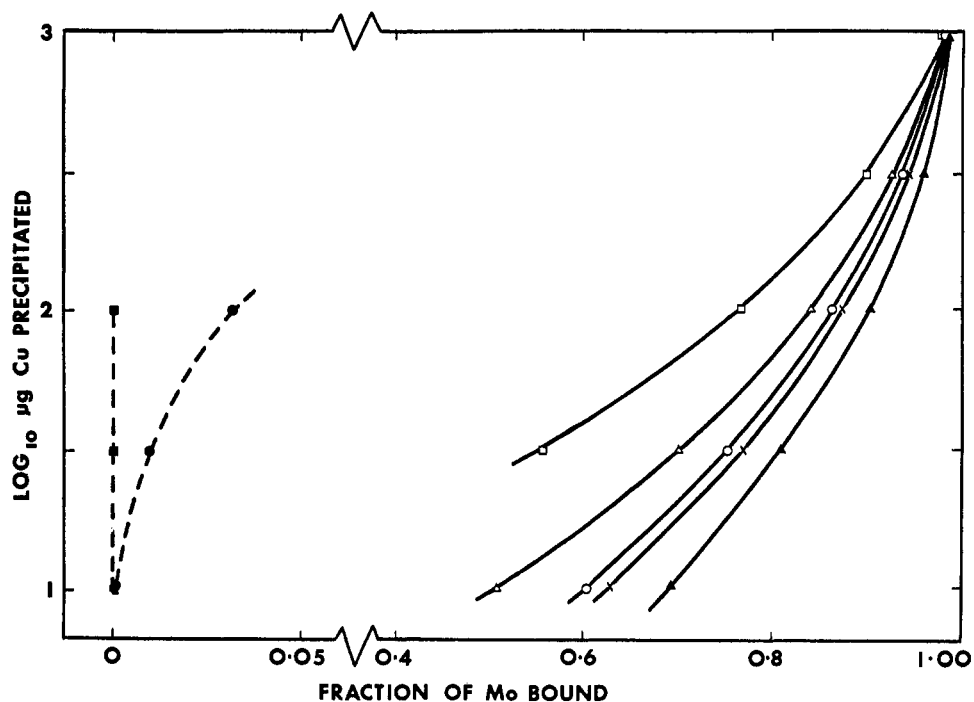(15) J. E. Allen, *Spectrochim. Acta*, **17**, 459–66 (1961).
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Figure 1. Binding of Mo by Cu dithiol complex precipitated from:

$0.5M$ —▲—▲—; $1M$ —✕—✕—; $2M$ —◯—◯—; $3M$ —△—△—; $5M$ —☐—☐—; $7M$ —●—●—; and 10 M HCl —■—■—. Data are means for 2.5, 5, and 10 μg Mo
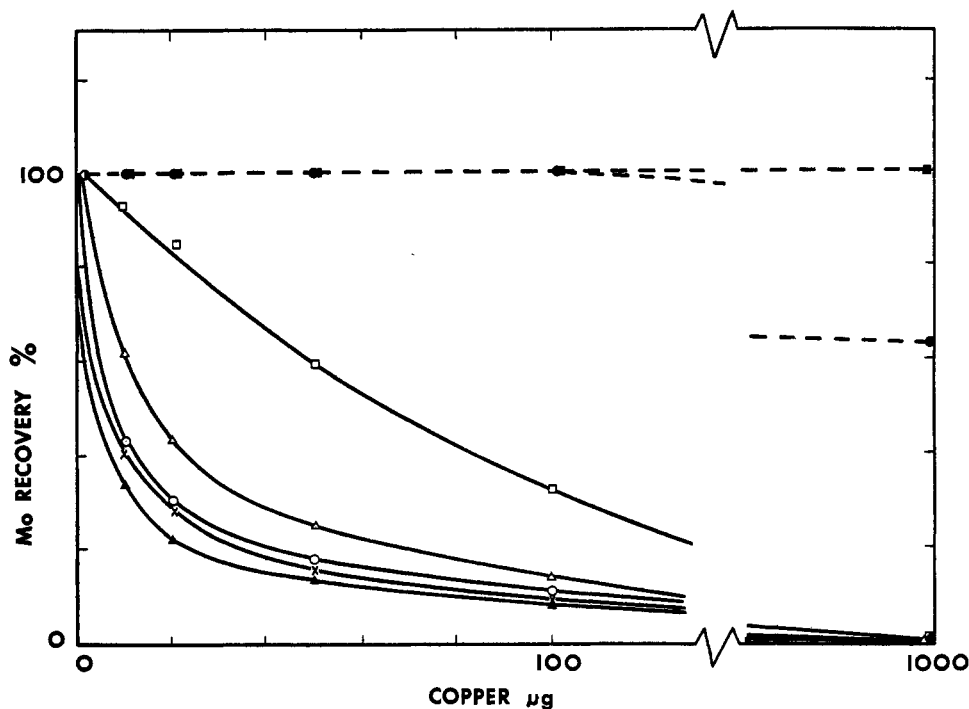
Figure 2. Effect of 0–1000 μg Cu on recovery of Mo from:

$0.5M$ —▲—▲—; $1M$ —✕—✕—; $2M$ —◯—◯—; $3M$ —△—△—; $5M$ —☐—☐—; $7M$ —●—●—; and $10M$ HCl —■—■—. Data are means for 2.5, 5, and 10 μg Mo

Interaction of Changes in the Concentration of HCl and Cu(II) with Recovery of MoD₃. The amount of copper precipitated and the HCl concentration at which precipitation occurred affected the recovery of MoD₃. Removal of Mo by the precipitated copper complex was confirmed by analysis. In all cases, copper in solution plus precipitated copper and extracted molybdenum plus copper-bound molybdenum were, respectively, equal to the amounts added.

At constant acid concentration, an increase in the quantity of precipitated copper complex was associated with a decline in the quantity of extracted MoD₃. The latter effect was not caused by depletion of the dithiol concentration as a large excess always remained. Under these conditions, copper-bound molybdenum was a constant fraction of the total Mo, therefore averaged results from the 2.5, 5, and 10 μg Mo additions are presented (Figure 1).

Extraction of a constant fraction of the total Mo demonstrated that the quantity bound was directly proportional to the initial concentration. This relationship is expressed: $Mo_{bound} = k \cdot Mo_{initial}$, where k is a constant which is increased by increasing the quantity of precipitated copper complex and decreasing the acid concentration. In $0.5M$ HCl, $0.7 < k < 1.0$ and in $10M$ HCl $0.000 < k < 0.005$ for all quantities of copper complex precipitated. The applicability of this model indicates that binding of molybdenum by the precipitate does not involve the formation of a mixed complex of specific stoichiometry.

Values interpolated from Figure 1 show that for a constant quantity of precipitated copper, the quantity of Mo bound was decreased by increasing the HCl concentration. This effect was greatest between 5 and $10M$ HCl. The large decrease in percentage copper precipitated, which occurred under the same conditions (Table I), suggests that there was a concomitant change in the physical characteristics of the precipitate or in the type of copper complex formed.

At HCl concentrations $>5M$, decreased Mo binding to copper dithiolate and decreased copper precipitation combined to cause a rapid decline of copper interference (Figure 2). This result is consistent with certain earlier reports (8, 13).

CONCLUSION

Copper(II) reduces the amount of extractable MoD_3 only if copper dithiolate is precipitated. The resulting loss of molybdenum is analytically significant for Cu to Mo ratios (w/w) as small as 1/1 in 0.5–$5M$ HCl (Figure 2). Higher acid concentrations increase the copper tolerance and with $10M$ HCl the interference is negligible at the highest Cu-to-Mo ratio tested (400/1).

Spectrophotometric Determination of Uranium(IV) with Potassium Iron(III) Cyanide

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REACTIONS such as the photoreduction of uranyl salt solutions in organic media result in the production of uranium(IV) in trace amounts. Typically, the uranium(IV) is accompanied by a large excess of uranyl ion and organic reagents in aqueous solution (1). This study was initiated to develop a rapid, simple uranium(IV) analysis under these conditions. A method developed by Nemodruk and Bezrogova utilizes Arsenazo(III), 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalene-disulfonic acid to form a colored complex with uranium(IV) after the latter has been extracted with tributyl phosphate (2). Our faster spectrophotometric procedure alleviates the necessity for extraction.

In our method, the aqueous U(IV) solutions are reacted with ferric ion (FeCl₃) in acid medium:

$$U^{4+} + 2Fe^{3+} + 2H_2O \rightarrow UO_2{}^{2+} + 2Fe^{2+} + 4H^+ \quad (1)$$

The resultant ferrous ion is then reacted with potassium ferricyanide to produce a dark blue complex, apparently $KFeFe(CN)_6$, potassium iron(II)-hexacyano ferrate(III), or $Fe_3[Fe(CN)_6]_2$, iron(II)-hexacyano ferrate(III). The small quantity of the complex so formed is a colloidal suspension which settles to the bottom of the vessel only after standing for several hours. Within the first several hours after the initial reaction, as well as for several hours thereafter upon shaking, the complex has the characteristics of a bluish solution, and is subject to reproducible spectrophotometric absorption of visible light. See Figure 1.
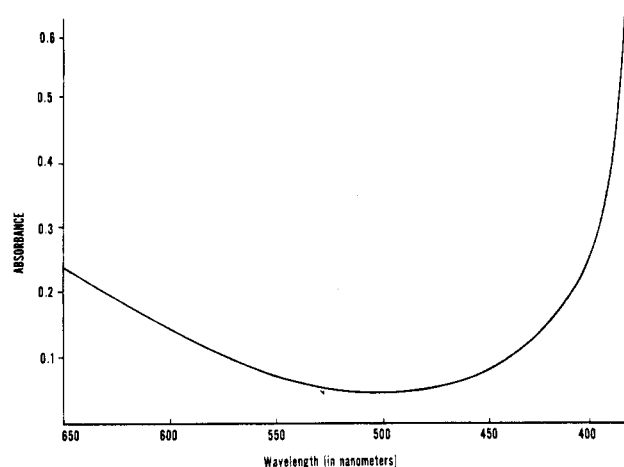

Figure 1. Visible region spectrum

Produced by reacting $1.414 \times 10^{-8}M$ (0.003365 mg/ml) U(IV) with ferric chloride and then complexing with potassium ferricyanide

EXPERIMENTAL

Reagents. DISTILLED WATER. Double distilled deoxygenated water was used to prepare all solutions.

STANDARD FERROUS AMMONIUM SULFATE SOLUTIONS. Stock solutions were prepared from weighed amounts of Baker and Adamson reagent grade ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$. The ferrous ion concentration was determined spectroscopically using the ortho-phenanthroline complex absorption at 510 nm or by titration with standard potassium dichromate solutions.

FERRIC CHLORIDE SOLUTIONS. Reagent grade Fisher ferric chloride, $FeCl_3 \cdot 6H_2O$ was dissolved in dilute hydro-

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