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**Summary**—The use of furfural thiosemicarbazone as a gravimetric reagent for palladium is described. The optimum analytical conditions for precipitation of the palladium complex and the effect of possible interferences have been investigated.

**Zusammenfassung**—Die Verwendung von Furfuralthiosemicarbazon als gravimetrisches Reagens für Palladium wird beschrieben. Die optimalen analytischen Bedingungen zur Fällung des Palladiumkomplexes und der Einfluß möglicher Störungen wurde untersucht.

**Résumé**—On décrit l'emploi de la thiosemicarbazone du furfural comme réactif gravimétrique pour le palladium. On a étudié les conditions analytiques optimales pour la précipitation du complexe du palladium et l'influence d'interférences possibles.

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## EXTRACTIVE SPECTROPHOTOMETRY OF THE MOLYBDENUM (III) 1,10-PHENANTHROLINE THIOCYANATE AND 2,2'-BIPYRIDYL THIOCYANATE COMPLEXES\*

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Komarowski and Poluektoff<sup>1</sup> observed that an acidic solution of molybdenum containing 2,2'-bipyridyl, when reduced with chlorostannous acid, gave a reddish violet colour. Moss *et al.*<sup>2</sup> later observed that the same reaction is given by 1,10-phenanthroline and tried to stabilize the colour of both complexes of reduced molybdenum, but were unsuccessful. They also observed that the phenanthroline reaction was the more sensitive but did not recommend the procedure, because of instability of the colour. Lazarev<sup>3</sup> stabilized the bipyridyl complex by reducing with chlorostannous acid in presence of tartaric acid, the molar absorptivity being  $1.8 \times 10^3$  l.mole<sup>-1</sup>.cm<sup>-1</sup> at 520 nm. The phenanthroline complex was studied qualitatively by Rao *et al.*,<sup>4</sup> who also found the molar absorptivity to be  $8.82 \times 10^3$  l.mole<sup>-1</sup>.cm<sup>-1</sup> at 565 nm.

It is now found that phenanthroline, bipyridyl and bathophenanthroline form stable complexes with molybdenum(III) in 1,2-dichloroethane in presence of chlorostannous acid and thiocyanate. An acidic solution of molybdenum containing thiocyanate and phenanthroline or bipyridyl is reduced with chlorostannous acid and the resultant precipitate extracted into 1,2-dichloroethane.

### EXPERIMENTAL

#### Reagents

**Standard molybdenum solution, 0.01%.** Prepared by dissolving MoO<sub>3</sub> (1.5 g) in a few ml of dilute sodium hydroxide solution, diluting to about 100 ml, making slightly acidic with dilute hydrochloric acid and then diluting to 1000 ml. It was diluted to 0.001 and 0.0001% with 0.1M hydrochloric acid.

**1,10-Phenanthroline monohydrate solution, 0.1%.**

**2,2'-Bipyridyl solution.** 2,2'-Bipyridyl (1 g) dissolved in the minimum necessary amount of 6M hydrochloric acid and diluted to 1000 ml.

**Bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) solution, 0.1% in ethanol.**

**Potassium thiocyanate solution, 20%.**

**Chlorostannous acid solution, 5%.** Stannous chloride (20 g) dissolved in 50 ml of concentrated hydrochloric acid and diluted to 400 ml. Metallic tin was added to prevent oxidation during storage.

All other reagents were analytical grade. Water and solvents were redistilled in glass apparatus.

#### Apparatus

**Silver reductor.** Prepared according to Vogel.<sup>5</sup>

\* Abstracted from a thesis presented by A. K. Bhadra to the University of Calcutta in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1970.

### Procedure

To a solution containing 0.06 mg of molybdenum, 5 ml of phenanthroline or bipyridyl or bathophenanthroline solution, 5 ml of methanol and 2 ml of potassium thiocyanate solution were added. The pH was adjusted to 1.5 and the solution transferred into a separating-funnel, followed by 5 ml of chlorostannous acid. After 1 min, the solution was shaken with 15 ml of 1,2-dichloroethane for about 20 min. The extraction was repeated with 5 ml of 1,2-dichloroethane, with shaking for 3 min. The extracts were collected in a 25-ml flask and diluted to volume with 1,2-dichloroethane. Turbidity was removed by the addition of 0.5 g of anhydrous sodium sulphate. The absorbance of the phenanthroline and bipyridyl complexes was measured at 525 nm and that of the bathophenanthroline complex at 565 nm, against a reagent blank.

When 2,2'-bipyridyl is used, addition of methanol may be omitted. For calibration curves, a 5-10 min equilibration is enough.

### RESULTS

The absorption spectra of the ternary complexes are shown in Fig. 1. The molar absorptivities *etc.* are given in Table 1.

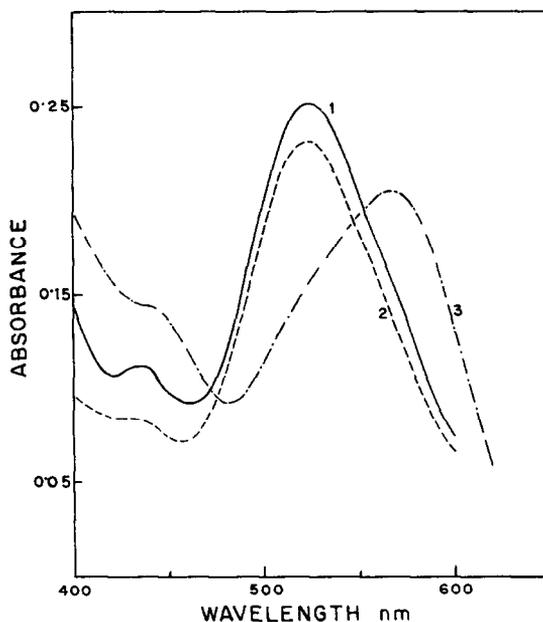


Fig. 1. Absorption spectra of the Mo(III)-1,10-phenanthroline thiocyanate (1), Mo(III)-2,2'-bipyridyl thiocyanate (2), and Mo-bathophenanthroline thiocyanate (3) complexes.

The optimum pH range of the aqueous solution before addition of chlorostannous acid is 1.2-6.5. If the pH is  $< 1.2$ , the colour of the complexes decreases.

The optimum thiocyanate concentrations in the aqueous phase for the phenanthroline, bipyridyl and bathophenanthroline systems are 0.25-1, 0.25-2, and 0.25-2M respectively. Thiocyanate added in excess causes colourless precipitates insoluble in 1,2-dichloroethane.

### Effect of methanol

Serious interferences due to phosphorus, tungsten, vanadium, silicon, aluminium *etc.* in the phenanthro-

Table 1. Characteristics of the extracts of the molybdenum(III) complexes

| Complex                          | Solvent            | $\lambda_{\max}$<br>nm | Molar absorptivity,<br>$l.\text{mole}^{-1}.\text{cm}^{-1}$ | Sandell<br>sensitivity<br>$\mu\text{g}/\text{cm}^2$ |
|----------------------------------|--------------------|------------------------|--|---|
| Mo(III)-phen-<br>thiocyanate     | 1,2-dichloroethane | 525                    | $9.52 \times 10^3$   | 0.010   |
| Mo(III)-phen-<br>thiocyanate     | chloroform         | 525                    | $6.46 \times 10^3$   | 0.014   |
| Mo(III)-bipy-<br>thiocyanate     | 1,2-dichloroethane | 525                    | $8.20 \times 10^3$   | 0.012   |
| Mo(III)-bipy-<br>thiocyanate     | chloroform         | 525                    | $5.88 \times 10^3$   | 0.016   |
| Mo(III)-bathophen<br>thiocyanate | 1,2-dichloroethane | 565                    | $8.16 \times 10^3$   | 0.012   |

line system can be overcome by addition of methanol to the aqueous solution before addition of chlorostannous acid. The effect is not understood but the addition of methanol is necessary, as the method completely fails in presence of aluminium, tungsten, *etc.* in absence of methanol. With the bipyridyl system, addition of methanol is not necessary.

Two or three drops of the chlorostannous acid solution have been found to be sufficient for reduction of molybdenum. In order to reduce the interference of iron, 2-5 ml of chlorostannous acid solution were used in all cases. A large excess decreases the colour of the complexes.

Beer's law is obeyed over the concentration ranges 1-10  $\mu\text{g}/\text{ml}$ , at 525 nm for the phenanthroline and bipyridyl systems, and at 565 nm for the bathophenanthroline complex.

#### Interference studies

To a solution containing 60  $\mu\text{g}$  of molybdenum, the interfering ions were added, followed by 15 ml of phenanthroline or bipyridyl solution, 2 ml of thiocyanate solution, 5 ml of methanol and 2-3 ml of chlorostannous acid solution and the mixture was extracted with 1,2-dichloroethane, with shaking for about 20 min. A deviation of <2% was regarded as indicating no interference. The results are summarized in Table 2.

Table 2. Effect of various ions on the phenanthroline and bipyridyl ternary complexes.

| Species            | Added as  | Tolerance limit, mg |
|--------------------|---|---------------------|
| Fe(III)            | $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ | 1.2                 |
| Al(III)            | $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$   | 100                 |
| W(VI)              | $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$        | 10.0                |
| V(V)               | $\text{V}_2\text{O}_5$                                    | 0.6                 |
| $\text{PO}_4^{3-}$ | $\text{NaH}_2\text{PO}_4$                                 | 10.0                |
| Silica             | Added after fusion with sodium carbonate                  | 10.0                |

#### Nature of the complexes

The oxidation state of molybdenum in the complexes was checked by comparing the complexes with those obtained by reaction of thiocyanate and phenanthroline or bipyridyl with molybdenum reduced to the trivalent state in 6M hydrochloric acid in a silver reductor at 60-80°.

Extraction took very much longer to complete (3-4 hr) than when the molybdenum was reduced in presence of the complexing agents. Only with reduction in 6M acid medium did the product have the same

characteristics as that obtained by the recommended procedure. Reduction in 2 or 4M acid gave erratic results and incomplete complex formation. A similar check was not possible for the bathophenanthroline complex, on account of the severe interference from traces of iron(II) produced in the reduction step. No attempt was made to determine the stoichiometry of the complexes.

## DISCUSSION

Because of its lower sensitivity and the serious interference from iron, the bathophenanthroline complex was not studied closely. The phenanthroline complex is poorly extracted in presence of interfering substances unless methanol is added before the extraction. The bipyridyl system is superior in this respect though somewhat less sensitive.

Several solvents were tried. In polar solvents, a pink red solution appears within a few minutes of shaking, but on standing the colour changes to yellow. The best solvent proved to be 1,2-dichloroethane.

The extraction is complete in a single pass with 1,2-dichloroethane. A 5-min equilibrium period is sufficient in absence of interfering elements but longer is needed in their presence. A blueish pink colour appears in the organic phase after shaking for a few seconds, and changes to reddish pink after 5–6 min shaking.

Binary complexes of molybdenum formed with phenanthroline, bipyridyl or bathophenanthroline in presence of chlorostannous acid are extractable into 1,2-dichloroethane, but are unstable. The phenanthroline and bipyridyl complexes have  $\lambda_{\text{max}}$  at 510–520 nm and the bathophenanthroline complex has  $\lambda_{\text{max}}$  at 540 nm. The molar absorptivities are  $2.72 \times 10^3$ ,  $1.8 \times 10^3$  and  $3.2 \times 10^3$  l.mole<sup>-1</sup>.cm<sup>-1</sup> respectively. It is not known whether chlorostannous acid is responsible for the extraction of the molybdenum complexes as in the case of ferroin.<sup>6</sup>

The sequence of addition of reagents is important. Colour development is extremely slow when a solution containing molybdenum and thiocyanate is shaken with 1,2-dichloroethane in presence of chlorostannous acid, followed by addition of phenanthroline, or bipyridyl, requiring an equilibration period of 3–4 hr. The yellow organic extract obtained by shaking for about 30 min, if left overnight in presence of the aqueous phase, changes to reddish pink with the correct absorbance. This probably indicates a rearrangement as suggested by Rao *et al.*<sup>4</sup>

We prefer the formula Mo(III)-1,10-phenanthroline(SCN)<sub>3</sub> to the MoO-1,10-phenanthroline(SCN)<sub>3</sub> suggested by Rao *et al.*,<sup>4</sup> as trivalent molybdenum is involved in the reaction.

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**Summary**—New extraction spectrophotometric methods for the determination of small amounts of molybdenum have been developed, using thiocyanate and 1,10-phenanthroline or 2,2'-bipyridyl as reagents in the presence of chlorostannous acid. Extracts of the ternary complexes of trivalent molybdenum in 1,2-dichloroethane obey Beer's law in the range 1–10  $\mu\text{g/ml}$  at 525 nm. A 10-fold excess of iron and vanadium and 100-fold excess of tungsten, phosphorus and silicate do not interfere.

**Zusammenfassung**—Neue extraktions-spektrophotometrische Methoden zur Bestimmung kleiner Molybdänmengen wurden entwickelt; sie verwenden Thiocyanat und 1,10-Phenanthrolin oder 2,2'-Bipyridyl als Reagentien in Gegenwart von Chlorozinn(II)-säure. Extrakte der ternären Komplexe von dreiwertigem Molybdän in 1,2-Dichloräthan gehorchen bei 525 nm im Bereich 1–10  $\mu\text{g/ml}$  dem Beerschen Gesetz. Ein 10-facher Überschub von Eisen und Vanadium und 100-facher Überschub von Wolfram, Phosphor und Silikat stören nicht.