

## Selective precipitation of Mo(VI) with $\alpha,\alpha'$ -bipyridine and 1,10-phenanthroline: Application to molybdenum and radiomolybdenum chemistry

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The purpose of this work was the selective precipitation of Mo(VI) with  $\alpha,\alpha'$ -bipyridine and 1,10-phenanthroline. This precipitation, not reported in the literature, was used for the separation of molybdenum from the elements co-eluted from an alumina microspheres column. The alumina had been loaded using a nitric acid solution from the dissolution of a U-Al target. The emphasis was placed on the Mo(VI) separation from ruthenium, tellurium and iodine, all of them were eluted as a group of anionic complexes from the alumina column.

### Introduction

A new procedure for the final purification of molybdenum used in nuclear medicine has been developed. The purpose of this work was the selective precipitation of Mo(VI) with  $\alpha,\alpha'$ -bipyridine (dipy) and 1,10-phenanthroline (phen). This precipitation was used especially for the separation of molybdenum from ruthenium, tellurium and iodine. These elements have been adsorbed together with molybdenum on a column of alumina microspheres from nitric acid solution after dissolution of an U-Al target.

The molybdenum generated by fission and separated by chromatography using alumina,<sup>1</sup> has, in general, not the required purity for use as technetium generator. Some radionuclides in form of anions, especially  $\text{TeO}_3^{2-}$ ,  $\text{RuO}_4^-$  and  $\text{I}^-$ , are adsorbed together with Mo(VI) from nitric acid into the alumina column. This made the introduction of some more steps necessary for molybdenum purification.

The reagent most studied for molybdenum purification via precipitation is  $\alpha$ -benzoinoxime. The separation and purification by molybdenum precipitation with  $\alpha$ -benzoinoxime<sup>2,3</sup> can be upgraded by ion exchange chromatography<sup>4</sup> and solvent extraction.<sup>5,6</sup> Molybdenum(VI) forms with  $\alpha$ -benzoinoxime a compound with the formula  $\text{MoO}_2(\text{C}_4\text{H}_{12}\text{O}_2\text{N}_2)$ .<sup>7</sup>

The heterocyclic complexes formed with the compounds  $\alpha,\alpha'$ -dipyridine and 1,10 phenanthroline have great importance in the coordination chemistry.<sup>8–16</sup>

DHINGRA and KAKKAR<sup>17</sup> described a method for molybdenum extraction with 1,10-phenanthroline in isobutyl-methyl ketone for spectrophotometric analysis of Mo(VI). The reaction is performed in the presence of stannous chloride. The same reaction is described for the determination of molybdenum with  $\alpha,\alpha'$ -dipyridine.<sup>18,19</sup>

SANDELL<sup>20</sup> used 1,10-phenanthroline as a sensitive reagent for the determination of iron and claimed that molybdenum(VI) does not interfere at pH over 5.5, but observed that the solution get a turbid aspect. Nevertheless, any relevance to the observed fact to be a possible precipitation of Mo(VI) by phenanthroline was not emphasized.

The purpose of this work is the separation of molybdenum from ruthenium, tellurium and iodine whose anionic complexes are adsorbed into the alumina column and are eluted as molybdate by ammonium chloride. The separation of molybdenum from ruthenium, tellurium and iodine is accomplished by the selective precipitation of molybdenum by 1,10-phenanthroline and/or  $\alpha,\alpha'$ -dipyridine. These precipitation reactions are not described in the literature.

The chemical composition and characterization of the obtained precipitates are described herein.

### Experimental

#### Reagents

Stock solution of molybdenum containing  $10 \text{ g}\cdot\text{l}^{-1}$  Mo was prepared by the dissolution of sodium molybdate dihydrate in demineralized water. Dilute solutions were prepared using this stock solution.

The reagents 1,10-phenanthroline and  $\alpha,\alpha'$ -dipyridine were dissolved in water and slightly acidified with hydrochloric acid to prepare  $10 \text{ g}\cdot\text{l}^{-1}$  each as stock solutions.

Stock solutions of the elements ( $10 \text{ g}\cdot\text{l}^{-1}$ ) given to molybdenum as sources of interference were prepared by dissolution of the correspondent chlorides.

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### *Precipitation of molybdenum*

The procedure for the precipitation of molybdenum with 1,10-phenanthroline and  $\alpha,\alpha'$ -dypiridine is the same. For each precipitation an aliquot containing 30 mg of Mo(VI) was used. The pH was adjusted with dilute  $\text{NH}_4\text{OH}$  or HCl. The influence of the pH on the precipitation was studied in the 0.1–8.0 range. All experiments were performed from room temperature (20–25 °C) until 100 °C and under constant stirring. In all experiments the solutions of the reagents were added to the molybdenum solution.

The precipitate was separated by filtration and washed with HCl solution of the same pH as the precipitation medium, followed by a washing with distilled water and finally with ethanol. The precipitates were dried in desiccators under vacuum for 96 hours.

### *Interference studies*

The elements studied as possible sources of interference were given as their chlorides to the molybdenum solutions before precipitation. A Mo/interference ratio of 1:1 was used in each experiment. Elements that could be fission products and could follow molybdenum were considered. The following elements were studied: Cs(I), Ba(II), Sr(II), Zn(II), Al(III), Dy(III), Fe(III), La(III), Nd(III), Pr(III), Ru(III), Sm(III), Y(III), Ce(IV), Te(IV), Zr(IV), U(VI) and Sb(III).

### *Characterization of compounds*

The compounds obtained by the precipitation of molybdenum with 1,10-phenanthroline and  $\alpha,\alpha'$ -dypiridine were characterized by solubility tests, gravimetry and X-ray fluorescence, elemental CHN analysis, thermogravimetry (TG) and differential thermogravimetry (DTG), infrared spectrophotometry and X-ray diffraction (powder method).

Determination of Mo(VI) in the filtrate was achieved by voltammetry with hanging mercury drop electrode in 0.5M tartaric acid as support electrolyte. That analysis was confirmed by inductively coupled plasma optical emission spectrometry (ICP/OES).

Burning the precipitate to a constant weight at a temperature of 550 °C and weighing the residue as  $\text{MoO}_3$  composed the gravimetric determination of molybdenum.

## **Results**

### *Preparation of compounds at different pH's*

To samples containing the same amount, about 30 mg of Mo as molybdate solution, aliquots of dypiridine and o-phenanthroline, dissolved in diluted solution of hydrochloric acid were added separately. The influence of the pH for the precipitation was studied in the 0.1–8.0 range. Both organic reagents showed the same behavior in the presence of molybdate. The best precipitation occurred in the 2–4 pH range, being the formed precipitates voluminous and easy to filter. For both reagents, the molybdenum(VI) precipitation was quantitative.

### *Temperature effect*

From ambient temperature (20–25 °C) to 50 °C, the precipitated compounds were white and voluminous. As the temperature raised and reached 100 °C, both precipitates became denser and a little lengthier to filter.

### *Solubility tests*

The Mo-dipy and Mo-phen compounds are insoluble in water, alcohol, acetone and hydrochloric acid. Both precipitates are sparingly soluble in carbon tetrachloride, ethyl ether, butyl acetate and acetic acid. Both compounds are freely soluble in concentrate solution of sulfuric and nitric acid and in ammonium hydroxide as well.

### *Interferences*

From the studied elements: Cs(I), Ba(II), Sr(II), Zn(II), Al(III), Dy(III), Fe(III), La(III), Nd(III), Pr(III), Ru(III), Sm(III), Y(III), Ce(IV), Te(IV), Zr(IV) and U(VI), all of them were not precipitated by both reagents. From the group elements studied as interference sources only Sb(III) is precipitated by 1,10-phenanthroline and  $\alpha,\alpha'$ -dypiridine, but the precipitates are soluble in excess of hydrochloric acid.

The XRF analysis of the precipitates obtained by both reagents detected only minor traces of the above elements used as spike for the molybdenum precipitation.

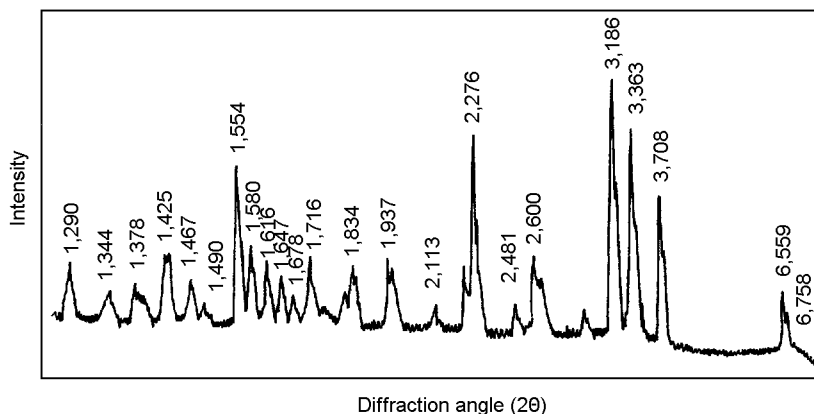


Fig. 1. Powder X-ray diffraction pattern of MoO<sub>3</sub> from Mo-phen

### Stoichiometric proposition

The stoichiometry for both compounds obtained by precipitation of molybdenum(VI) with 1,10-phenanthroline and  $\alpha,\alpha'$ -dipyridine was established using the data of gravimetric and elemental CHN analyses. For the gravimetric determination of molybdenum as MoO<sub>3</sub>, the dried precipitates were calcinated at 550 °C. The stoichiometries proposed are C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>·MoO<sub>3</sub>·H<sub>2</sub>O, for the compound formed with Mo(VI) and o-phenanthroline (Mo-dipy) and C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>·MoO<sub>3</sub> for the compound formed with Mo(VI) and  $\alpha,\alpha'$ -dipyridine (Mo-dipy). Analyses using TG, DTG and IR also confirmed these stoichiometries.

Figure 1 shows the diffractogram, (powder method), for MoO<sub>3</sub>, obtained by calcination of the compound Mo(VI)-1,10-phenanthroline at 550 °C. Similar diffractograms were obtained for Mo-dipy.

### Conclusions

In a previous work<sup>21</sup> the authors demonstrated a novel precipitation reaction using alizarine blue (7,8-dihydroxy-5,6-phthalquinoline) as a sensitive, specific and quantitative precipitant for molybdenum. In the present paper the authors report and confirm their findings that molybdenum is completely and quantitatively precipitated from low acidic solutions by the reagents 1,10-phenanthroline and  $\alpha,\alpha'$ -dipyridine.

The precipitation of molybdenum(VI) with both 1,10-phenanthroline or  $\alpha,\alpha'$ -dipyridine had a similar behavior. At the pH range 0–1, the precipitate was very fine, presented some difficulty for filtration and was adherent to the walls of the porous glass filter. In the pH range of 2–4, the precipitate was voluminous, quickly formed and easily filtered. In the pH range 5–6 the precipitate was gelatinous and the filtration is lasted.

At the pH range of 6–7 the precipitation was not complete, only turbidity formed. Finally, at pH ≥ 8 there was no precipitation at all. The recommended pH for the precipitation is, therefore, 3.

The precipitation performed from room temperature (20–25 °C) to 50 °C led to voluminous white precipitates which could be easily filtered. As the temperature was raised up to 100 °C, the precipitates became denser and exhibited some filtration difficulty. Molybdenum was analyzed in the filtrate by voltammetry method with hanging mercury drop electrode, and ICP/AES. The analysis confirmed that the precipitation was quantitative when using both precipitants.

The solubility tests performed with Mo-1,10-phenanthroline and Mo- $\alpha,\alpha'$ -dipyridine led to the conclusion that the precipitates are insoluble in water, ethanol, acetone and hydrochloric acid. They are slightly soluble in carbon tetrachloride, ether, butyl acetate and acetic acid. They are completely soluble in concentrated solutions of sulfuric and nitric acids and in ammonium hydroxide. As a consequence of the solubility of both precipitates in nitric acid, the immediate precipitation of Mo(VI) with the studied precipitants is not allowed for the solutions resultant from the target dissolution. Its pH must be ascertained before precipitation.

The molybdenum compound precipitated with o-phenanthroline had a molecular mass (CHN analysis) of 342. The stoichiometry proposed is C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>·MoO<sub>3</sub>·H<sub>2</sub>O. For the precipitate compound with molybdenum and  $\alpha,\alpha'$ -dipyridine, the molecular mass was 302 and the stoichiometry proposed is C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>·MoO<sub>3</sub>. IR, TG and DTG analyses confirmed these results.

The molybdenum precipitation with 1,10-phenanthroline or  $\alpha,\alpha'$ -dipyridine was obtained at ambient temperature and formed a white, voluminous and not hygroscopic powder when dried. The

precipitation was selective, only Sb(III) precipitated by both reagents when the molybdenum solution had a lower acidity than that used in this work.

Both compounds Mo- $\alpha,\alpha'$ -dypiridine and Mo-1,10-phenanthroline can be burned to MoO<sub>3</sub> and the oxide submitted to further purification by sublimation.

### Application

The precipitation reaction of Mo(VI) using 1,10-phenanthroline or  $\alpha,\alpha'$ -dypiridine is selective and quantitative. It was applied to the separation and recovery of molybdenum eluted from an alumina microspheres column, simulating the separation of fission radiomolybdenum, in the purification of <sup>99</sup>Mo for a technetium generator.

### References

1. F. M. S. CARVALHO, A. ABRÃO, J. Radioanal. Nucl. Chem., 218 (1997) 259.
2. E. M. SCADDEN, Nucleonics, 15 (1957) No. 4, 102.
3. E. A. C. CROUCH, G. B. COOK, J. Inorg. Nucl. Chem., 2 (1956) 223.
4. W. L. CHENG, C. S. LEE, C. C. CHEN, V. M. WANG, G. TING, Appl. Radiation Isotopes, 40 (1989) 315.
5. N. BLAGOJEVIC, R. E. BOYD, E. L. R. HIETHERINGTON, Intern. J. Appl. Radiation Isotopes, 36 (1985) 85.
6. C. K. SIVARAMAKRISHNAN, A. V. JADHAV, K. RAGHURAMAN, S. RAMAN, P. S. NAIR, M. V. RAMANIAH, Preparation of High Purity Fission Produced Molybdenum-99, BARC-847, 1976.
7. H. J. HOENES, K. G. STONE, Talanta, 4 (1960) 250.
8. F. BASOLO, J. C. HAYES, H. M. NEUMANN, J. Am. Chem. Soc., 76 (1954) 3807.
9. C. CRENTZ, M. CHOU, T. L. NETZEL, M. OKUMURA, N. SUTIN, J. Am. Chem. Soc., 102 (1980) 1309.
10. E. AMOUYAL, A. HOMSI, J. Chem. Soc. Dalton Trans., 1841 (1990).
11. J. K. NAGLE, J. S. BERNSTEIN, R. C. YOUNG, T. J. MEYER', Inorg. Chem., 20 (1981) 1760.
12. L. E. BENNETT, H. TAUBE, Inorg. Chem., 7 (1968) 254.
13. R. G. PEARSON, O. A. GANSOW, Inorg. Chem., 7 (1968) 1373.
14. E. KONIG, S. HERZOG, J. Nucl. Chem., 32 (1970) 585.
15. F. BASOLO, J. C. HAYES, H. M. NEUMANN, J. Am. Chem. Soc., 75 (1953) 5102.
16. E. KONIG, S. HERZOG, J. Inorg. Nucl. Chem., 32 (1970) 613.
17. U. DHINGRA, L. R. KAKKAR, Analyst, 113 (1988) 675.
18. A. S. KOMAROVSKII, N. S. POLUEKTOV, Mikrochim. Acta, 1 (1937) 264.
19. J. GILLIS, Mikrochim. Acta, 31 (1943) 58.
20. E. B. SANDELL, Colorimetric Determination of Traces of Metals, Interscience Publishers, Inc., New York, N.Y., 1944.
21. F. M. S. CARVALHO, E. A. ABRÃO, Anais da Assoc. Bras. Quím., 44 (1995) No. 2, 1.