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**NUCLEAR SCIENCE SERIES**

**The Radiochemistry  
of Molybdenum**



**U.S.  
Atomic  
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# **The Radiochemistry of Molybdenum**

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and

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## FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences-National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, the problems of stockpiling uncontaminated materials, the availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman  
Subcommittee on Radiochemistry





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## INTRODUCTION

This volume which deals with the radiochemistry of molybdenum is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the elements as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of molybdenum which might be included in a revised version of the monograph.

I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF MOLYBDENUM

"A Comprehensive Treatise on Inorganic and Theoretical Chemistry", J. W. Mellor, Vol. XI, Chapter LXI, Longmans, Green and Co., New York (1931)

"Analytical Chemistry of the Manhattan Project", C. J. Rodden and J. C. Warf, pp. 450-455, McGraw-Hill Book Co., New York (1950)

"Applied Inorganic Analysis", Hillebrand, Lundell, Bright and Hoffman, 2nd ed., "Molybdenum", pp. 302-316, John Wiley and Sons, Inc., New York (1953)

"Fritz Ephraim Inorganic Chemistry", P. C. L. Thorne and E. R. Roberts, Chapter 18, 6th ed., rev., Nordeman Publishing Co., Inc., New York (1954)

"Gmelin's Handbuch der Anorganischen Chemie", System No. 53, 8th ed., Verlag Chemie, G.M.B.H. Berlin (1935)

"Molybdenum Compounds", D. H. Killeffer and A. Linz, Interscience Publishers, New York (1952)

"Outlines of Methods of Chemical Analysis", G.E.F. Lundell and J.I. Hoffman, John Wiley and Sons, Inc., New York (1938)

"Qualitative Analysis for the Rare Elements", A.A. Noyes and W.C. Bray, The Macmillan Co., New York (1948)

"Reference Book of Inorganic Chemistry", W.M. Latimer and J.H. Hildebrand, 3rd ed., The Macmillan Co., New York (1951)

"Scott's Standard Methods of Chemical Analysis", N.H. Furman, Editor, 5th ed., Vol. I, "Molybdenum", pp. 585-613, D. Van Nostrand Co., Inc., New York (1939)

"Treatise on Inorganic Chemistry", H. Remy, Vol. II, Elsevier Publishing Co., New York (1956)

## II. TABLE OF ISOTOPES OF MOLYBDENUM

Isotope	Half life	Type of Decay	Method of Preparation
Mo <sup>90</sup>	5.7 hr	$\beta^+$ , EC	Nb <sup>93</sup> (p,-) Mo <sup>90</sup>
Mo <sup>91m</sup>	66 sec	IT (57%), $\beta^+$ , EC	Mo <sup>92</sup> ( $\gamma$ , n) Mo <sup>91m</sup>
Mo <sup>91</sup>	15.5 min	$\beta^+$ , No $\gamma$	Mo <sup>92</sup> ( $\gamma$ , n) Mo <sup>91</sup> Mo <sup>92</sup> (n, 2n) Mo <sup>91</sup>
Mo <sup>93m</sup>	6.95 hr	IT	Nb <sup>93</sup> (d, 2n) Mo <sup>93m</sup> Nb <sup>93</sup> (p, n) Mo <sup>93m</sup>
Mo <sup>93</sup>	> 2 yrs	EC	same as Mo <sup>93m</sup>
Mo <sup>99</sup>	66.0 hr	$\beta^-$ , $\gamma$	fission Mo <sup>98</sup> (n, $\gamma$ ) Mo <sup>99</sup> Mo <sup>100</sup> ( $\gamma$ , n) Mo <sup>99</sup>
Mo <sup>101</sup>	14.6 min	$\beta^-$ , $\gamma$	fission
Mo <sup>102</sup>	11.5 min	$\beta^-$	fission
Mo <sup>105</sup>	< 2 min	$\beta^-$	fission

See "Table of Isotopes" by D. Strominger, J. Hollander and G. Seaborg, Reviews of Modern Physics 30, No. 2, Part II, April 1958 for more information concerning decay schemes, daughter products, etc. and for references to the original literature.

## III. REVIEWS OF THOSE FEATURES OF MOLYBDENUM CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS

### 1. Metallic Molybdenum and Molybdenum Trioxide

Molybdenum is a hard metal; grey in powder form and silvery in appearance in compact form. It has a density of 10.2 and its melting point is about 2620°C. The potential ( $E_P^0$ ) for the Mo-Mo(VI) couple is + 1.05 volts.<sup>1</sup> Methods of preparation of the metal include reduction of molybdenum trioxide with hydrogen or carbon or reduction of ammonium molybdate with hydrogen. Surface oxidation of the metal proceeds slowly at room temperature.

The metal is soluble in dilute nitric acid, warm aqua regia or hot concentrated sulfuric acid. Concentrated nitric acid renders the metal passive.

It is insoluble in concentrated hydrochloric acid, hydrofluoric acid (though soluble in a mixture of nitric and hydrofluoric or sulfuric acids), cold concentrated sulfuric acid, dilute sulfuric acid, or for all practical purposes aqueous potassium or sodium hydroxide. Fusion with potassium nitrite, -nitrate, -chlorate, sodium peroxide, or sodium carbonate plus potassium nitrate, oxidizes the metal to a soluble molybdate.

Molybdenum trioxide,  $\text{MoO}_3$ , is a white powder, slightly soluble in water, readily soluble in caustic alkalis, ammonium hydroxide or in alkaline solutions generally. Ignited molybdenum oxide is soluble in hydrofluoric or concentrated sulfuric acid. Molybdic oxide melts at  $791^\circ\text{C}$ . According to T. Dupuis and C. Duval,<sup>2</sup> the oxide does not sublime below  $780^\circ\text{C}$ . These authors report reagents, weighing forms and temperature limits for the ignition of various compounds of molybdenum. S. C. Liang and K. N. Chang<sup>3</sup> recommend ignition of molybdic oxide at  $500\text{--}550^\circ\text{C}$  for analytical purposes.

Methods of preparation of molybdenum trioxide include oxidation of the metal or molybdenite ( $\text{MoS}_2$ ) by ignition in air or by decomposition of molybdates with acids such as nitric or hydrochloric.

## 2. Soluble Compounds of Molybdenum

Molybdenum has six oxidation states: 0, +2, +3, +4, +5, and +6. The +6 oxidation state is the one most commonly found in aqueous solution. Molybdenum is generally considered to exist in solution as an oxygenated anion in the +6 state. It is easily reduced by the usual reducing agents such as zinc, stannous chloride, sulfur dioxide, hydrazine, etc. Under controlled conditions, i.e., in neutral or slightly acid solution, mild reduction of molybdenum(VI) will produce molybdenum blue, otherwise molybdenum(III) is the usual end product. It is not yet known what the exact nature of the blue intermediate reduction product is, whether it is a mixture of the +6 and +5 or the +6 and +4 oxidation states.

Molybdenum(III) is very sensitive to oxidation and must be protected from air (oxygen) and other oxidizing substances.

When molybdenum(VI) is reduced with mercury, molybdenum blue is not produced but the product of the reduction is molybdenum(V) which is also susceptible to air oxidation. The +5 state can be partially stabilized by the presence of a complexing ion such as thiocyanate.

Water soluble compounds of molybdenum(VI) include the ammonium, sodium, potassium and magnesium salts of normal molybdates.

### 3. Insoluble Compounds of Molybdenum

Table I lists the ordinary insoluble compounds of molybdenum. The normal molybdates are generally all readily soluble in acids.

Silver and lead molybdate, molybdenum cupferrate, 8-hydroxyquinolate and  $\alpha$ -benzoinoximate have all been used in the gravimetric determination of molybdenum in radiochemistry.

The precipitating properties of these reagents for molybdenum, the fission products and other elements which may be present in the solution will be briefly reviewed. Detailed discussions concerning their use in analysis will be found in the references in Part I.

Lead molybdate: The gravimetric determination of molybdenum as lead molybdate is a commonly employed procedure in radiochemistry. The molybdate is precipitated from hot, weakly acid solution by the addition of lead nitrate. The precipitate may be dried at  $110^{\circ}$  or ignited to red heat. Lead molybdate is preferable to silver molybdate because conditions for precipitation (absence of chloride and sulfate ion) are not as critical.

Molybdenum cupferrate: Molybdenum is precipitated from a fairly strong acid solution by cupferron (nitrosophenylhydroxylamine). However, cupferron is not a selective reagent for molybdenum as it will also precipitate many of the fission products, e.g., Zr, Nb, Pd, etc., U(IV) (but not U(VI)) and other elements. Therefore it is useful as a precipitant for the determination of the yield of molybdenum only in solutions where these elements are not present or are preferentially complexed. The cupferrate can be ignited and molybdenum determined as molybdenum trioxide.

TABLE I. INSOLUBLE COMPOUNDS OF MOLYBDENUM

INORGANIC			
Reagent	Precipitate	Solubility in Water	Solubility in Other Reagents
Ag <sup>+</sup>	Ag <sub>2</sub> MoO <sub>4</sub>	.0044 gms/100 mls(25°)	s. HNO <sub>3</sub> , KCN, NaOH, NH <sub>4</sub> OH solns.
Ba <sup>+2</sup>	BaMoO <sub>4</sub>	.0058 gms/100 mls(23°)	sl. sol. in acid
Bi <sup>+3</sup>	Bi <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	.02 gms/100 gms	v. sol. in acids
Ca <sup>+2</sup>	CaMoO <sub>4</sub>	insoluble	s. acids, i. alcohol and ether
Cd <sup>+2</sup>	CdMoO <sub>4</sub>	sl. soluble	s. acids, NH <sub>4</sub> OH, KCN
Hg <sub>2</sub> <sup>+2</sup>	Hg <sub>2</sub> MoO <sub>4</sub>	insoluble	
La <sup>+3</sup>	La <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	sl. soluble	s. acids
Pb <sup>+2</sup>	PbMoO <sub>4</sub>	insoluble	d. conc. H <sub>2</sub> SO <sub>4</sub> , s. acids, KOH, i. alcohol
Sr <sup>+2</sup>	SrMoO <sub>4</sub>	.0104 gms/100 mls(17°)	s. acids
Th <sup>+4</sup>	Th(MoO <sub>4</sub> ) <sub>2</sub>	insoluble	s. acids
S <sup>=</sup>	MoS <sub>3</sub>	insoluble	s. NH <sub>4</sub> OH, alkaline sulfides

## ORGANIC

Reagent	Precipitated from	Soluble in
cupferron*	1-2M HCl or H <sub>2</sub> SO <sub>4</sub>	6N HNO <sub>3</sub> <sup>†</sup> , 6N NH <sub>4</sub> OH
8-hydroxyquinoline	buffered acid solution, e.g., acetic acid-acetate	mineral acid
α-benzoinoxime	1M acid solutions	fuming HNO <sub>3</sub> , NH <sub>4</sub> OH + H <sub>2</sub> O <sub>2</sub>

\* nitrosophenylhydroxylamine.

† organic material partially oxidized.

Molybdenum oxinate: 8-hydroxyquinoline (oxine) as a reagent for molybdenum has the same property as cupferron, i.e., it precipitates a large number of elements from a slightly acid or alkaline solution. According to Fribil and Malat<sup>4</sup>, molybdenum can be separated from Fe(III), Al, Be, Zn, Ni, Co, Mn, Pb,

Cd, Bi, Cu and Hg(II) by precipitation of molybdenum oxinate from an ammonium acetate-acetic acid buffered solution containing the di-sodium salt of EDTA (ethylenediaminetetraacetic acid). Tungsten (VI), V(V) and U(VI) also precipitate. Titanium must be removed before precipitation. Malinek<sup>5</sup> states that V can be held in solution by reducing it to V(II) and then complexing it with EDTA at pH 1-2. Molybdenum oxinate may be dried at 40-270° and weighed as  $\text{MoO}_2[\text{C}_9\text{H}_6\text{ON}]_2$ .<sup>2</sup>

Molybdenum  $\alpha$ -benzoinoximate: Alpha-benzoinoxime is practically a specific reagent for molybdenum.<sup>6</sup> Only W, Pd, V(V), Nb, Ta and Cr(VI) interfere in the precipitation of molybdenum from 1 M acid solution by the addition of an alcoholic solution of the reagent. Chromium and vanadium can be reduced to lower valence states in which they do not precipitate. Niobium, W, Ta and Pd must be removed. In fission product chemistry, niobium is removed as the hydrated oxide with iron as carrier. Palladium radioactivity is so insignificant in comparison to the molybdenum activity in low energy fission that no special procedure is required to remove it.

Molybdenum oximate may be ignited and weighed as molybdic oxide.

Molybdenum sulfide: Molybdenum sulfide is generally not used in the gravimetric determination of molybdenum in radiochemistry, for there are far better methods available. It has been employed as a means of separating molybdenum from the fission products which do not form sulfides in acid solution.<sup>7,8</sup>

Molybdenum sulfide is precipitated by passing  $\text{H}_2\text{S}$  through the acid solution containing molybdenum or by acidifying a thiomolybdate solution. Molybdenum sulfide should not be weighed as such because its composition is generally indefinite. ( $\text{H}_2\text{S}$  reduces some of the molybdenum to lower oxidation states.) Also, according to Duval<sup>9</sup>, there is no plateau in the thermogravimetric curve until the sulfide has been converted to molybdic oxide. The sulfide should be ignited carefully and weighed as molybdic oxide.

Coprecipitation of molybdenum: Several methods are mentioned here which, while not dealing specifically with tracer amounts of molybdenum, were used to



separate, presumably quantitatively, microgram quantities of molybdenum, and therefore might be applicable to the carrying of tracer molybdenum.

Picket and Hankins<sup>10</sup> made a study of the co-precipitation of molybdenum, cobalt and copper, in tracer and  $\mu\text{gm.}$  amounts, as the 8-hydroxyquinolates with indium or aluminum as carriers. Precipitation was from an ammonium acetate buffered solution at pH 5.2. Aluminum or indium oxinate alone carried 85 per cent or more of the molybdenum present. In the presence of oxine plus tannic acid and thioanilide, aluminum or indium carried better than 95 per cent of the molybdenum.

Niobium, tellurium and molybdenum are specifically removed from a solution of the fission products which is more than 10  $M$  in nitric acid by co-precipitation on manganese dioxide.<sup>11</sup> Park<sup>12</sup> reported the practically quantitative carrying of 0.1-2 mgs. molybdenum, antimony and bismuth on manganese dioxide from one liter of boiling solution by the addition of potassium bromide and potassium permanganate. The procedure was used for separating trace impurities from copper.

Pohl<sup>13</sup> employed the ammonium salt of pyrrolidine-dithiocarbamate, with thallium(I) as carrier, for precipitating a large number of trace impurities, including molybdenum, away from aluminum.

Scharrer and Eberhardt<sup>14</sup> precipitated 100 mgs. of bismuth as the sulfide to carry molybdenum as a preliminary separation in the determination of trace amounts of molybdenum in soils, plants and animal products. Molybdenum may be collected on other acid-insoluble sulfides such as antimony or copper.

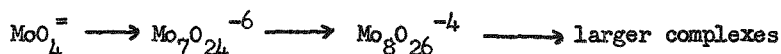
Ultramicro quantities of molybdenum(VI) are quantitatively co-crystallized from slightly acid aqueous solutions with  $\alpha$ -benzoinoxime. An acetone solution of the reagent is added to the aqueous solution containing molybdenum at such concentration that the solution remains homogeneous. The solution is boiled to drive off the acetone whereupon, the oxime, due to its low solubility in water, crystallizes out carrying molybdenum with it.<sup>15</sup>

Molybdenum may be separated from these matrices by dissolution or destruction of the precipitate, by solvent extraction, ion exchange techniques, precipitation of the carrier or a combination of these methods.

#### 4. Complex Ions of Molybdenum

Molybdenum chemistry is very complex and, as yet, not thoroughly understood or investigated. The possession of six oxidation states (including the 0 state) does not simplify matters. Apparently a small change in the conditions, i.e., temperature, pH, concentrations, etc., of a particular system under investigation can sometimes markedly affect this system. This has led to a good deal of confusion and contradiction in the literature concerning molybdenum species, oxidation states involved and equilibria.

It is generally believed that the principal molybdenum species existing in alkaline solution is the simple molybdate ion  $\text{MoO}_4^{2-}$ . On acidifying such a solution, i.e., lowering the pH past 7, molybdate ions condense to form polymolybdate ions. Lindqvist,<sup>16</sup> on the basis of spectrophotometric studies has proposed the following sequence:



Molybdenum has a strong capacity for forming complex anions. Besides the isopolymolybdates, molybdenum forms (a) heteropoly acids, complexes of molybdic acid with phosphoric, silicic, telluric acids, etc., (b) peroxy-molybdates, compounds or complexes of molybdates with hydrogen peroxide, (c) complexes in the (VI) and lower oxidation states with halides, cyanide, thiocyanate, etc., and (d) complexes or compounds with many organic substances, such as oxalic acid, citric acid, thioglycollic acid, phenyl hydrazine, catechol, EDTA, 1,10-phenanthroline, etc.

While many complexes or compounds, both organic and inorganic, are known, there is very little definite quantitative information available concerning their strengths or even their formulae.

Nelidow and Diamond<sup>17</sup> studied the behavior of molybdenum in various solvent extraction systems. They proposed the formula  $\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_y(\text{Ether})_z$ , where X represents a halide ion, for the species extracting into diethyl or diisopropyl ether from 3-9 M HCl or 6 M HBr, and also discussed at length the possible factors involved in the mechanism of this solvent extraction system. Diamond,<sup>18</sup>

in a series of papers, has extended this study to the development of a general expression for the distribution coefficient of a metal halide between an aqueous hydrohalic acid phase and an organic solvent and has tested the validity of this expression for the extraction of molybdenum(VI) and indium(III). Some information was obtained concerning the aqueous molybdenum(VI) species; polymeric forms can exist at hydrohalic acid concentrations below 6 M (and < 0.1 M molybdenum); the main species are apparently the anions of acids stronger than HCl.

Perrin<sup>19</sup> investigated the nature of the molybdenum thiocyanate complex. Through spectrophotometric studies in 60% acetone-water solutions, he concluded that in 1M hydrochloric acid, molybdenum(V) forms thiocyanate complexes in which the ratio Mo:CNS is 1:3, 1:2 and 1:1 for high, moderate and low concentrations of thiocyanate respectively. The 1:3 complex is amber, fairly stable, uncharged and probably  $\text{MoO}(\text{CNS})_3$ ; this is the colored complex used in chemical analysis. The 1:2 complex is yellow and unstable. The 1:1 complex is colorless. The logs of the association constants for the complexes in 60% acetone-water at 20-30° and ionic strength 1.07-1.10, are 1.85, 3.01 and 3.2 for the 1:3, 1:2 and 1:1 complexes, respectively.

## 5. Chelate Compounds of Molybdenum

Molybdenum forms many chelate complexes or compounds. Some have been used in molybdenum radiochemistry, but their use has not been extensive.

Many molybdenum chelate complexes or compounds have been employed in analytical chemistry for the separation and/or determination of molybdenum in a wide variety of materials and some of these chelates should be useful in the radiochemistry of molybdenum.

A brief discussion of a few molybdenum chelate complexes will show their broad application.

Precipitation with cupferron, 8-hydroxyquinoline and  $\alpha$ -benzoinoxime has already been mentioned (III, Part 3).

Acetylacetone is a 1,3-diketone which possesses the fairly unique characteristic of being both chelating agent and solvent and certain extractions

may be carried out from high acid concentrations with it. Molybdenum, as  $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ , can be quantitatively extracted from 6 N sulfuric acid by a 1:1 mixture of acetylacetone and chloroform.<sup>20</sup>

Molybdenum(VI), tungsten(VI) and rhenium(VII) in acid solution react with toluene-3,4-dithiol to form chelate compounds that are soluble in butyl or amyl acetate and carbon tetrachloride.<sup>21,22</sup> Gilbert<sup>23</sup> found that there are three dithiol molecules to each molybdenum atom in the complex and also, that when molybdenum(V) is treated with dithiol, the (V) complex disproportionates between the molybdenum(VI) complex and a molybdenum(IV) complex; the ratio of the (VI)/(IV) complexes depends on the acidity. Molybdenum(III) does not react. Molybdenum may be separated from tungsten by inhibiting the formation of the tungsten complex through control of the acid concentration or the addition of citric acid.<sup>24-26</sup> Many procedures have been devised for the colorimetric determination of molybdenum with dithiol in steel<sup>24,25,27</sup>, drugs<sup>26</sup>, plants<sup>28,33</sup>, soils and rocks<sup>29-31</sup>, uranium<sup>32</sup> and animal tissues<sup>33</sup>.

Ethylenediaminetetraacetic acid (EDTA) forms chelate complexes in acid solution with molybdenum(VI) and (V) in which there are two atoms of molybdenum to each molecule of EDTA. The EDTA complex holds molybdenum in the (V) oxidation state in solution at pH < 7. The formulas for the (VI) and (V) complexes are  $\text{Na}_4\text{Mo}_2\text{O}_{22}\text{H}_{28}\text{C}_{10}\text{N}_2$  and  $\text{Na}_2\text{Mo}_2\text{O}_{13}\text{H}_{14}\text{C}_{10}\text{N}_2$  respectively.<sup>34</sup> Molybdenum is held in solution by the di-sodium salt of EDTA while uranium(IV) is precipitated by cupferron at pH 4-6.<sup>35</sup> However, EDTA does not affect the extraction of molybdenum(VI) by 8-hydroxyquinoline into chloroform at pH 1.6-5.6.<sup>36</sup> Also, as pointed out in Section III,3, precipitation of molybdenum oxinate from an ammonium acetate-acetic acid buffered solution containing the di-sodium salt of EDTA serves to separate Mo from a large number of other elements.<sup>4</sup>

The compounds of molybdenum with cupferron<sup>37,38</sup> (separation from rhenium)<sup>39</sup> and  $\alpha$ -benzoinoxime<sup>40</sup> are soluble in chloroform. The extraction of molybdenum with  $\alpha$ -benzoinoxime is the first step in a rapid spectrophotometric determination of the element in thorium oxide, uranyl sulfate and steel.<sup>41</sup>

Molybdenum may be separated from most metals in the presence of sodium fluoride or EDTA in 0.1-0.5 N hydrochloric acid by extraction with Morin into 1-butanol.<sup>42</sup>

Molybdenum forms complexes with sodium diethyldithiocarbamate<sup>43</sup> (soluble in chloroform), xanthate<sup>44</sup> (separation from rhenium)<sup>45</sup> and di-sodium-1,2-dihydroxy-3,5-benzenedisulfonate (Tiron).<sup>46</sup> The Tiron complex is the basis of a very sensitive colorimetric (aqueous) procedure for molybdenum.

## 6. Solvent Extraction

The extraction of molybdenum from an aqueous solution into an organic solvent has been studied by many investigators for many different systems. A few of these have been briefly mentioned in Part 5: Chelate Compounds of Molybdenum.

Relatively little information is available in the literature concerning the extraction of radioactive molybdenum. However, there are numerous references for the determination of microgram quantities of molybdenum in soils, plants, steels, alloys, "pure" metals, etc. which employ solvent extraction as a means of determining the element colorimetrically or spectrographically. Again, reference to these methods may prove helpful to the radiochemist. "Colorimetric Methods of Analysis" by Snell and Snell<sup>47</sup> and "Colorimetric Determination of Traces of Metals" by Sandell<sup>48</sup> provide excellent coverage of this subject.

Two classical methods which have been employed in the separation of fission product molybdenum are the extraction of the thiocyanate or chloride complexes of molybdenum into diethyl ether.

Thiocyanate: Molybdenum in dilute acid in the presence of a reducing agent, such as stannous chloride, forms a red-colored complex with thiocyanate. This reaction has been used for many years as a means of determining molybdenum colorimetrically. Hiskey and Meloche,<sup>49</sup> in a study of the complex, stated that it was formed with molybdenum(V), and that the ratio of thiocyanate to molybdenum was 3:1. R. Bock<sup>50</sup> has made a detailed investigation of the

extraction of various metal thiocyanates at 0.1 M concentrations into ethyl ether from 0.5 M hydrochloric acid solutions which were 1 to 7 M in ammonium thiocyanate. By varying the ammonium thiocyanate concentration, volume ratios, etc., molybdenum can be separated from a number of fission products, uranium(VI) and other elements.

The molybdenum(V) complex is soluble in such solvents as amyl alcohol, butyl acetate, iso-propyl ether, ethyl acetate and cyclohexanol. Goto and Ikeda<sup>51</sup> studied the extraction of molybdenum thiocyanate by various organic solvents for spectrophotometric purposes; ethyl acetate or iso-butyl alcohol and its mixture with chloroform or carbon tetrachloride were suitable solvents.

Wilkinson and Grummitt<sup>8</sup> incorporated the extraction of molybdenum(V) thiocyanate as a step in a procedure for separating molybdenum from uranium and other fission products. Molybdenum sulfide was precipitated, dissolved in aqua regia and the molybdenum extracted from 4 M hydrochloric acid solution into ethyl ether as the thiocyanate complex (Zn was the reducing agent). Molybdenum was back extracted with 8 M hydrochloric acid, and, after evaporation of the aqueous extract and treatment of the residue with nitric acid, was precipitated twice as lead molybdate.

Molybdenum can be separated from rhenium, vanadium and chromium by using mercury as the reducing agent (rhenium is not reduced) and then extracting the molybdenum(V) thiocyanate complex with butyl acetate (the colored vanadium and chromium reduction products are not soluble in butyl acetate).<sup>52</sup> In the presence of sodium fluoride and EDTA, molybdenum is separated from titanium and other metals by extraction of the thiocyanate complex by a 1:1 mixture of carbon tetrachloride and amyl alcohol.<sup>53</sup>

Ethyl Ether: Molybdenum will extract into ethyl ether from halogen acid solutions. Swift<sup>54</sup> reported 80-90% extraction from 6 M HCl. Other investigators report 54, 9.7 and 6.5 per cent extraction from 6 M HBr<sup>55</sup>, 3.5 M HF<sup>56</sup> and 6.9 M HI<sup>57</sup> solutions, respectively.

Stout and Meagher<sup>58</sup> prepared "carrier-free" Mo<sup>93,99</sup>, which had been produced in an ( $\alpha$ ,n) reaction with zirconium, by ether extraction. The zirconium target was dissolved in 12 N H<sub>2</sub>SO<sub>4</sub>, the solution evaporated to fumes, then diluted with water and the chloride and hydrogen ion concentrations adjusted to 6 M. Molybdenum was then extracted quantitatively with diethyl ether.

Wiles and Coryell<sup>59</sup> used ether extractions to separate molybdenum from fission product mixtures. Molybdenum was extracted from 6 M HCl, back extracted from the ether phase with water, the aqueous phase was scavenged with a ferric hydroxide precipitate and molybdenum precipitated as the 8-hydroxyquinolate for mounting and counting. See Procedure C in Section VI in this report.

A rapid separation of molybdenum and technetium from fission products and each other was effected by extracting molybdenum(VI) with ether from a 6 M HCl solution of irradiated uranium, precipitating the molybdenum with 8-hydroxyquinolate and separating or milking the technetium from molybdenum by precipitating nitron pertechnetate with rhenium as the carrier.<sup>60</sup>

Comparison of Solvents: Nelidow and Diamond<sup>17</sup> conducted an extensive investigation of the extraction behavior of molybdenum(VI), using Mo<sup>99</sup> and Mo<sup>93m</sup> tracers, from aqueous halogen acid solutions into various ketones, esters, ethers, an alcohol and some non-oxygenated solvents. The original paper should be consulted for detailed information. A very brief resumé of some of the results of their investigation follows.

The non-oxygenated solvents, carbon tetrachloride, chloroform, etc. were extremely poor extractants for molybdenum(VI). Of the oxygenated solvents, the ketones, esters and the alcohol were all better extractants than the corresponding ether; the order being: esters and alcohol > ketones > ether. The nature of the halogen acid affected the extraction of molybdenum. In general, extractions from hydrobromic acid solutions were better and from hydrofluoric acid solutions were worse than extractions from hydrochloric acid solutions. The effect of temperature was also noted: better extractions were obtained at 5° than at 45° with the exception of extractions by the alcohol (2-ethylhexanol) which seemed to be independent of the temperature in the range examined.

Varying the initial concentration of molybdenum in the aqueous phase from  $10^{-9}$  M to  $10^{-2}$  M did not affect the distribution coefficients for the two solvents tested (hexone and  $\beta,\beta'$ -dichlorodiethyl ether).

Table II is a representative list of the solvents with which distribution coefficients, D,  $[(\text{Mo}) \text{ org.}/(\text{Mo}) \text{ aq.}]$  greater than 10 were observed at room temperature.

Table II

Solvent	Aqueous Phase	D
Methyl isobutyl ketone (hexone)	6 M HCl	20
" " "	7 M HCl	29
" " "	5 M HBr	17
Diisopropyl ketone	7 M HBr	29
Isoamyl acetate	7 M HCl	18
$\beta,\beta'$ -dichlorodiethyl ether	9 M HBr	~25

Yamamoto<sup>61</sup> studied the extraction of molybdenum from 2-7 M hydrochloric acid by ether, amyl alcohol, amyl acetate, butyl acetate and their binary mixtures. The 1:1 mixtures of ether with butyl acetate, amyl alcohol or butyl alcohol extracted over 90% of the molybdenum. When the solvents were tested separately butyl acetate was the best extractant: 82.5% of the molybdenum extracted from 5.4 M hydrochloric acid. When the temperature for the extraction was dropped to 10°, over 99% of the molybdenum was extracted by butyl acetate from 7.5 M hydrochloric acid.

Methyl isobutyl ketone (hexone): Waterbury and Bricker<sup>62</sup> devised a procedure for the determination of .01-1.0% molybdenum in plutonium and plutonium alloys. An aliquot of the dissolved sample containing 100 $\gamma$  or less of molybdenum is made 6 M in hydrochloric acid and 0.4 M in hydrofluoric acid. The solution is contacted three times with equilibrated hexone and the molybdenum in the combined organic phases is back-extracted with three portions of water. Molybdenum is then determined in the aqueous phase colorimetrically with chloranilic acid after freeing the combined extracts from hydrofluoric acid



by evaporation with concentrated acid and from iron by precipitation of the hydroxide from dilute alkaline solution.

Tributyl Phosphate (TBP): TBP is an excellent extractant for molybdenum. Nelidow and Diamond<sup>17</sup> report distribution coefficients  $\left[ \frac{(\text{Mo})_{\text{org.}}}{(\text{Mo})_{\text{aq.}}} \right]$  from 1 M and 2 M hydrochloric acid solutions of 4.0 and 65 respectively with D increasing with increasing acid concentration. Gerlit<sup>63</sup> reports distribution coefficients of 8.5 and 21.6 from neutral medium and 2 N sulfuric acid solutions respectively.

TBP and hexone are used for the solvent recovery of uranium and plutonium. Under various conditions, both also extract thorium, neptunium and fission products such as ruthenium, zirconium, and cerium; TBP can also extract the rare earths.<sup>64,65</sup>

Other Solvents: Other classes of solvents which may prove useful in the solvent extraction of molybdenum are the mono- and di-alkylphosphates, the di- and tri-alkylphosphine oxides, and the simple primary, secondary and tertiary amines. While there are no references to the use of these solvents in the radiochemical analysis of molybdenum, some of them should be quite helpful. A few examples will give some idea of their possibilities.

More than 99% of the molybdenum(VI) was extracted from uranium leach liquors by 0.4 M DDPA (mono ester of dodecylphosphoric acid) in kerosene.<sup>66</sup>

Extraction coefficients of  $>1000$  were observed for molybdenum(VI) when sulfuric acid solutions (pH 2) containing  $\sim 3$  mgs Mo/ml were contacted with an approximately equal volume of 0.1 M solutions of the amines, e.g., 1-(3-ethylpentyl)-4-ethyloctylamine, dilaurylamine, methyl dilaurylamine, in an aromatic hydrocarbon diluent. However, these amine extractions have the characteristic that as the concentration of molybdenum in the aqueous phase decreases, so does its distribution coefficient.<sup>67</sup>

White<sup>68</sup> studied the extraction behavior of over forty elements with the trialkylphosphine oxides. Molybdenum(VI) was completely extracted from 1 M hydrochloric or sulfuric acid solutions by 0.1 M tri-n-octylphosphine

oxide in cyclohexane and partially extracted from the same aqueous media by 0.1 M tris-2-ethylhexylphosphine oxide.

Several papers concerning the extraction of other elements with these solvents were presented at the Second United Nations International Conference on the Peaceful Uses of Atomic Energy. Morrison and Freiser<sup>69</sup> provide a summary of the extraction of various elements, including molybdenum, by tri-alkylphosphine oxides and high molecular weight amines.

## 7. Chromatographic Behavior of Molybdenum

### Anion Exchange

#### Hydrochloric acid

Molybdenum(VI) is adsorbed very strongly onto strong base anion resins (Dowex-1 and 2, Amberlite IRA-400) at low HCl concentrations ( $K_d$  1000-2000 at ~0.1 M HCl). As the HCl concentration increases,  $K_d$  drops to a minimum (10-20) at 1.5 M HCl, rises to a maximum (100-250) at 5 M HCl and then very slowly decreases.<sup>70-73</sup> The dip in the  $K_d$  curve indicates that there are possibly two species of molybdenum present at low HCl concentrations.

Thus molybdenum can be separated from elements which are not adsorbed strongly at high HCl concentrations. Kraus and Nelson<sup>74</sup> have compiled data for the adsorption from hydrochloric acid solutions onto Dowex-1 for essentially all the elements in the periodic table. The alkali metals, alkaline earths, rare earths, yttrium, actinium, thorium, nickel and aluminum are not adsorbed from HCl solutions.

Uranium, neptunium, plutonium(VI) and (IV), niobium and tungsten are adsorbed strongly from > 6 M HCl, zirconium from > 8 M HCl and protactinium from > 10 M HCl. Americium is not adsorbed from HCl solutions.

On the other hand, molybdenum should be separable from elements that are adsorbed strongly from 1-2 M HCl. Huffman, Oswalt and Williams<sup>72</sup> separated molybdenum from technetium on a Dowex-1 column (3 mm x 21 mm), chloride form. Molybdenum was removed quantitatively by elution with 1 M HCl and technetium was then removed with 4 M  $\text{HNO}_3$ .

### Nitric, sulfuric and phosphoric acids

Distribution coefficients have been determined for the adsorption of molybdenum and other elements onto Dowex-2 from nitric<sup>73</sup>, sulfuric<sup>73</sup> and phosphoric<sup>75</sup> acid solutions. Molybdenum is adsorbed very strongly from all three acids at 0.1 N acid concentration and then the adsorption drops rapidly with increasing acid concentration.

At 0.1 N  $\text{HNO}_3$ ,  $K_d$  is 500 and then drops with increasing acid concentration to 0.4 at 11 N  $\text{HNO}_3$ . Yttrium, Sr, Ce, Am and Nb are not adsorbed; Th, U(VI) and Zr are not adsorbed below 1 N  $\text{HNO}_3$  and all three peak around 8 N  $\text{HNO}_3$ . For protactinium,  $K_d$  at 0.1 N  $\text{HNO}_3$  is 3, stays fairly constant to 1 N  $\text{HNO}_3$  and then rises to a peak at 8 N  $\text{HNO}_3$ . Ruthenium behaves like molybdenum, but its adsorption drops much less rapidly.

In sulfuric acid, the  $K_d$  for molybdenum is 10,000 at 0.1 N  $\text{H}_2\text{SO}_4$  and drops to 11 at 12.5 N  $\text{H}_2\text{SO}_4$ . Niobium, U(VI), Zr and Pa behave similarly though none have as high a  $K_d$  in dilute  $\text{H}_2\text{SO}_4$  as molybdenum. Strontium, Y, Ce and Am did not show any significant adsorption. Thorium and Ru have relatively low  $K_d$ 's in dilute acid; adsorption drops to a minimum at 1-2 N  $\text{H}_2\text{SO}_4$  and then rises again. Thorium adsorption shows a peak at ~11 N  $\text{H}_2\text{SO}_4$ .

Molybdenum has a  $K_d$  of ~60,000 in 0.1 N  $\text{H}_3\text{PO}_4$ ; the  $K_d$  decreases rapidly to 4 at ~12.5 N  $\text{H}_3\text{PO}_4$ . Zirconium, Nb, U(VI) and Np behave similarly. Cesium and Te(IV) distribution coefficients are less than 1 and Ce and Sr distribution coefficients are less than 10 from 0.1 N to 12 N  $\text{H}_3\text{PO}_4$ .

Buchanan, et al., studied the adsorption of sixty elements onto Dowex-1 from nitric acid media. They found that molybdenum(VI) is not adsorbed from 1 N to 14 N  $\text{HNO}_3$ .<sup>76</sup>

### Hydrochloric-hydrofluoric acid

The adsorption behavior of molybdenum in HCl-HF-anion exchange systems has been studied by several investigators. The presence of fluoride ion has made possible several separations which were not feasible in hydrochloric acid solutions.

Hague, Brown and Bright<sup>77</sup> determined conditions for the separation of titanium, tungsten, molybdenum and niobium from each other on Dowex-1 (8-10 per cent cross linkage) with HCl-HF solutions.

Kraus, Nelson and Moore<sup>71</sup> separated molybdenum, tungsten and uranium from each other on a Dowex-1 column (10 per cent cross linkage, 200-230 mesh). The three elements were put on the column in 0.5 M HCl-1 M HF, uranium was eluted with 0.5 M HCl-1 M HF, tungsten was removed next with 9 M HCl-1 M HF and molybdenum was eluted last with 1 M HCl.

Wish<sup>78</sup> has combined elutions with HCl-HF,  $H_3PO_4$  and  $HNO_3$  to provide a method for the rapid, carrier-free separation of Np, Pu, U, Zr, Nb, Te and Mo from each other and their quantitative recovery from mixed fission product solutions on Dowex-2 (see Procedure D, Section VI in this report).

Barnes and Lang<sup>79</sup> (see Procedure B, Section VI in this report) and Stevenson, Hicks and Levy<sup>80</sup> have developed procedures for the radiochemical determination of molybdenum(VI) from mixed fission product solutions using ion-exchange techniques. Their procedures are briefly: adsorption of molybdenum(VI) from 6 M HCl onto an ion exchange resin, washing the resin with various eluants, stripping molybdenum off the resin with 6 M NaOH or 6 M ammonium acetate, scavenging the molybdenum-containing effluent with ferric hydroxide and then precipitation of molybdenum for yield determinations and counting.

#### Other Media

The behavior of rhenium and molybdenum on IRA-400, chlorate form, (IRA-400 is a strong base anion resin) with potassium oxalate has been incorporated into a procedure for the separation of macro quantities of molybdenum from rhenium. The elements are loaded onto the resin from an alkaline solution, molybdenum is removed with 1 M potassium oxalate and rhenium is stripped off with 1 M  $HClO_4$ .<sup>70</sup>

Molybdenum target material was separated from Tc<sup>99</sup> on IRA-400, chlorate form, by stripping off the molybdenum with  $K_2C_2O_4$ -KOH mixture and then eluting with Tc<sup>99</sup> with 0.5 M  $NH_4SCN$ .<sup>81</sup>

Blasius, Pittak and Negwer<sup>82</sup> report a rather unique procedure for the separation of mg. amounts of tungsten from molybdenum by taking advantage of

a small-pored Permutit-ES resin, chloride form. The tungstoborate ion is formed in the presence of molybdate by addition of  $H_3BO_3$  and NaOAc at pH 5.8. The aqueous solution of the crystalline slurry is adjusted to 5 N HCl. This solution is then passed through the column of Permutit-ES resin. Molybdenum is adsorbed, but the tungstoborate ion, due to its large size, cannot penetrate the pores of the resin and thus passes through the column. Molybdenum is eluted with NaOAc.

#### Cation Exchange

The question of the existence of a cationic species of molybdenum(VI), such as  $MoO_2^{+2}$ , has not been settled. Diamond<sup>83</sup> reports that there was little or no adsorption of molybdenum on Dowex-50 (cation resin) from 1-12 M HCl or 1-6 M HBr, HF,  $H_2SO_4$  or  $HNO_3$  solutions but that from 1-6 M  $HClO_4$  there was slight adsorption on the cation resin.

#### Paper Chromatography

The technique of paper chromatography has not been extensively employed for radiochemical separations. However a large number of systems have been studied for other purposes and a great variety of separations can be made. Reviews of the subject have been prepared by Weil<sup>84</sup> and Wells.<sup>85</sup>

An example of molybdenum separation by paper chromatography is that of Mo(III) in dilute HCl by use of the developer n-butanol saturated with 2 N  $HNO_3$  and 2 N HCl.<sup>86</sup> Molybdenum is separated from U, V, Cr, Mn, Fe, Co, Ni and Cu by this method.

Molybdenum(V) can be separated from molybdenum(VI) by filter paper chromatography with a mixture of con.  $HCl:H_2O:ether:MeOH$  in the ratio 4:15:50:30<sup>87</sup> or by ascending paper chromatography with the solvent  $H_2O$ -acetic acid - KSCN.<sup>88</sup>

Almasy and Straub<sup>89</sup> developed a specific separation for molybdenum from cations by ascending paper chromatography with the solvent EtOH-con.  $HCl-H_2O$  (4:1:5). Blasius and Czekay<sup>90</sup> separated molybdenum from tungsten (as their oxalate complexes) by paper chromatography with EtOH- $CHCl_3$ - 10 per cent aqueous

oxalic acid (7:2:1) as the mobile phase. Lederer<sup>91</sup> separated  $\text{Re}^{186}\text{O}_4^-$  from  $\text{MoO}_4^-$  and  $\text{Tc}^{99}\text{O}_4^-$  from  $\text{MoO}_4^-$  with a mixture of butyl alcohol with  $\text{N HCl}$ ,  $1.5 \text{ N HNO}_3$  or  $1.5 \text{ N}$  aqueous ammonia as the eluant.

Kertes and Lederer<sup>92</sup> published a list of  $R_F$  values for over fifty ions, including molybdate, for ascending paper chromatography with five different mixtures of  $\text{BuOH:HBr:H}_2\text{O}$  on Whatman No. 1. The  $R_F$  value is defined as the distance travelled by the zone divided by the distance travelled by the liquid front.

Thorough coverage of the subject of paper chromatography and its application in the field of inorganic chemistry is provided by Lederer and Lederer<sup>93</sup> and Block, Durrum and Zweig.<sup>94</sup>

## 8. Electrochemical Behavior of Molybdenum

The behavior of molybdenum in polarography, controlled potential electrolysis, and constant current mercury cathode electrolysis is of some interest in radiochemical separations. However the use of these techniques has been rather limited with molybdenum and they have had no significant use in radiochemical studies of this element. A recent review of the subject of controlled potential electrolysis is included by Lingane in his comprehensive book on electro-analytical chemistry.<sup>95</sup> A useful tabulation of elements which can be electro-deposited by the constant current mercury cathode technique is given by Lundell and Hoffman.<sup>96</sup> An excellent review of this subject has also been given by Maxwell and Graham.<sup>97</sup> A more recent detailed examination of the deposition in a mercury cathode of approximately twenty elements is reported by Bock and Hockstein.<sup>98</sup> They found 0.35 per cent of the molybdenum remaining in the aqueous phase after electrolysis of a  $0.1 \text{ N H}_2\text{SO}_4$  solution for 1.5 hours.

D. Love<sup>99</sup> describes a procedure for determining fission product  $\text{Mo}^{99}$ , which, while not directly involving molybdenum, is of interest.  $\text{Tc}^{99m}$  the daughter product of  $\text{Mo}^{99}$  decay, is amalgamated with Hg through selective polarographic reduction at a dropping Hg electrode. The amalgam is counted and  $\text{Mo}^{99}$  activity determined by making the appropriate corrections.

#### IV. DISSOLUTION OF SAMPLES FOR RADIOACTIVE MOLYBDENUM DETERMINATIONS

One of the problems the radiochemist must deal with in the dissolution of a sample for a radiochemical determination is assurance that exchange between the added inactive carrier and the radioisotopes of the element to be determined is complete.

If the radioactive isotope can be present in several oxidation states at the same time, one or more of which are difficult to oxidize or reduce, if it tends to form colloids or polymeric species, or if equilibrium rates between different species are slow, etc., exchange may be difficult to obtain.

In the case of molybdenum, treatment of the sample with strong oxidizing agents such as nitric acid, concentrated sulfuric acid, bromine, or strong oxidizing fluxes will generally achieve exchange and oxidize molybdenum to the +6 oxidation state.

However, a word of caution about the use of perchloric acid. Molybdenum apparently exists to a certain extent in a species in perchloric acid that is quite different from the species existing in nitric, sulfuric, hydrochloric acids, etc., and which behaves differently from these other species in some of the chemical reactions involved in molybdenum radiochemical separations. Thus if perchloric acid has been used in the dissolution of the sample it has been found advantageous to remove it by fuming with concentrated sulfuric acid before performing any subsequent chemistry.<sup>100</sup>

For dissolution procedures for a wide variety of samples for the determination of molybdenum, consult Snell and Snell's "Colorimetric Methods of Analysis"<sup>47</sup> and Sandell's "Colorimetric Determination of Traces of Metals".<sup>48</sup>

#### V. COUNTING TECHNIQUES FOR RADIOACTIVE MOLYBDENUM

Molybdenum<sup>99</sup> is generally the only radioactive isotope of molybdenum isolated from mixed fission product solutions; the other molybdenum fission product isotopes are very short lived, of the order of minutes or less.

Molybdenum<sup>99</sup> has a 66.0-hour half-life and decays via a 1.18-Mev  $\beta^-$  (83 per cent) to technetium<sup>99m</sup>. Technetium<sup>99m</sup> has a 6.0-hour half-life and decays via  $\gamma$  emission to technetium<sup>99</sup> which has a long half-life,  $\sim 2 \times 10^5$  years.

The activity of molybdenum<sup>99</sup> may be measured by either a beta- or gamma-counter. In the latter case it is necessary to allow the technetium<sup>99m</sup> daughter activity to reach equilibrium with the parent activity before counting. However, if the activity is measured in a beta-counter, an aluminum absorber of approximately 13 mg/cm<sup>2</sup> may be used to remove the conversion electrons from technetium<sup>99m</sup> and the sample may be counted immediately instead of waiting for equilibrium to be reached.

## VI. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR MOLYBDENUM

### MOLYBDENUM

#### PROCEDURE A

##### INTRODUCTION

This procedure for the radiochemical determination of Mo in fission product mixtures is based on precipitation reactions and is derived from the procedures of Ballou<sup>101</sup> and Scadden.<sup>102</sup> The main steps are precipitations of Mo with  $\alpha$ -benzoinoxime, precipitate dissolution and removal of coprecipitated impurities on ferric hydroxide, followed by precipitation of  $\text{PbMoO}_4$  for chemical yield determination and counting. Precision of individual determinations is about 1 per cent (standard deviation), and purities are greater than 99 per cent. Chemical yields are about 75 per cent and four determinations can be made in about 4 hours.

If tungsten is present, it will not be separated from Mo by this procedure. Interference by V or Cr, if present, can be eliminated by reducing them with  $\text{H}_2\text{SO}_3$  prior to precipitation of Mo with  $\alpha$ -benzoinoxime.<sup>103</sup>

##### PROCEDURE

1. Ten mg. of molybdenum(VI) are added to the sample in a 40-ml.



PROCEDURE A (Cont'd)

centrifuge tube, and the volume is adjusted to 30 ml. and the acidity to approximately 1  $N$  (Note 1). Five ml. of 2 per cent  $\alpha$ -benzoinoxime in ethanol are added, and the mixture stirred, then centrifuged at high speed. The precipitate is washed with 30 ml. of water.

2. The precipitate is dissolved in 3 ml. fuming  $HNO_3$ ; the solution is diluted to 25 ml. with water, partially neutralized with 1-2 ml. of conc. ammonium hydroxide, and cooled in an ice bath.
3. The molybdenum is reprecipitated by adding 5 ml. of the oxime reagent. The mixture is stirred and centrifuged. The precipitate is washed with 30 ml. of water.
4. Steps 2 and 3 are repeated.
5. The precipitate of Step 4 is dissolved in 3 ml. of fuming nitric acid. Three ml. perchloric acid are added. The solution is boiled to perchloric acid fumes (caution!) and then fumed almost to dryness (Note 2). Then the mixture is cooled.
6. Ten ml. of water and 1 mg. of ferric ion are added; ammonium hydroxide is added until the molybdic oxide dissolves and ferric hydroxide has precipitated. The mixture is filtered through any fast filter paper such as Whatman 4 or 41.
7. The filtrate is neutralized with 6  $N$   $HNO_3$  (litmus paper) and 1.5 ml. more of 6  $N$   $HNO_3$  is added. One ml. of  $Pb(NO_3)_2$  solution (100 mg.  $Pb^{+2}$ /ml) is added and the solution heated to boiling. If a precipitate starts to form one drop conc.  $NH_4OH$  is added, while if no precipitate appears two drops conc.  $NH_4OH$  are added. The solution is then boiled for several seconds only (Note 3). The solution is filtered hot through a weighed disc of Whatman 42 filter paper and the precipitate is washed with three 5 ml. portions of hot water and one 2-3 ml. portion of anhydrous methyl

## PROCEDURE A (Cont'd)

alcohol. The precipitate is dried at 105-110°C for 15 min., cooled in air for 20 min., weighed, and mounted for counting (Note 4).

### NOTES

1. If the previous history of the sample is such (e.g., reduced) that exchange between carrier and radioactive atoms may be incomplete, digestion with conc.  $\text{HNO}_3$  is necessary. In addition, the presence of fluoride interferes with subsequent steps and should be removed by fuming with about 1 ml. conc.  $\text{H}_2\text{SO}_4$ .
2. Much frothing occurs on boiling down the molybdenum oximate-fuming nitric acid-perchloric acid solution, and care must be exercised to prevent loss of solution from the tube.
3. The  $\text{PbMoO}_4$  precipitate formed in this way yields a reproducibly uniform sample for beta-ray counting. This is desirable since beta-ray counting characteristics of a sample are sensitive to such factors as precipitate clumping and compacting.
4. If beta-ray counting of  $\text{Mo}^{99}$  is to be done, an Al absorber (about 13 mg/cm<sup>2</sup>) can be used to remove the conversion electrons of 6.0-hr  $\text{Tc}^{99\text{m}}$  and thus eliminate the necessity of waiting for it to grow into equilibrium.

### PREPARATION AND STANDARDIZATION OF CARRIER

Dissolve 18.4 g.  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 1 liter  $\text{H}_2\text{O}$ . Standardize by withdrawing quadruplicate aliquots of 5.00 ml. and to each aliquot add 80 ml.  $\text{H}_2\text{O}$  and 2.5 ml. glacial  $\text{HC}_2\text{H}_3\text{O}_2$ . Warm almost to the boiling point, add 5.3 ml. of 4 per cent  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  solution dropwise and let stand for several minutes. Filter through a tared fine sintered glass crucible, wash precipitate with three 15 ml. portions hot  $\text{H}_2\text{O}$  and with 5 ml. anhydrous  $\text{CH}_3\text{OH}$ . Dry at 105-110°C for 15 min., cool in air 20 min., weigh. Repeat drying process to constant weight.

## MOLYBDENUM

### PROCEDURE B

#### INTRODUCTION

This procedure for the radiochemical determination of Mo in fission product mixtures is based largely on anion exchange resin separations as described by Barnes and Lang.<sup>79</sup> Another anion exchange procedure which also isolates Mo very effectively has been given by Stevenson, Hicks, and Levy<sup>80</sup> and differs in some of the eluants used. The main steps in the following procedure are adsorption of Mo on a column of Dowex-1 anion exchange resin from 5-9M HCl, removal of impurities by elutions with 6 M HCl, 0.1 M HCl-0.05 M HF, and 3 M NH<sub>4</sub>OH, elution of Mo with 6 M NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, precipitation of ferric hydroxide for additional decontamination, precipitation of Mo with  $\alpha$ -benzoins oxime, and ignition of this precipitate to MoO<sub>3</sub> for chemical yield determination and counting. Precision of individual determinations is better than 1 per cent (standard deviation), and purities are greater than 99 per cent. Chemical yields are about 75 per cent and eight determinations can be performed in about 4 hours.

If tungsten is present, it will not be removed by the procedure (nor by that of Stevenson, Hicks, and Levy).

#### PROCEDURE

1. Add the sample to 3.0 ml. of Mo carrier in a 40-ml. short-taper conical centrifuge tube. Add 1 ml. of Br<sub>2</sub>-H<sub>2</sub>O (Note 1) and bring to a boil over a burner. (If the volume is greater than 10 ml., the solution should be evaporated to 5 to 10 ml. in a 125-ml. Erlenmeyer flask.) Add sufficient conc. HCl to make the solution 5 to 9 M in this acid (Note 2).
2. Heat the solution to boiling, transfer to the Dowex-1 anion resin column (Note 3 and 4), and permit to run through under gravity. Add 1 to 2 ml. of 6 M HCl to the column, and when the level of acid reaches the top of the resin, add 10 ml. of

PROCEDURE B (Cont'd)

- hot HF-HCl solution (Note 5). When the level of the HF-HCl solution reaches the top of the resin, add 5 ml. of 3 M  $\text{NH}_4\text{OH}$ .
3. As soon as the level of the  $\text{NH}_4\text{OH}$  reaches the top of the resin, all effluents collected to this point are placed in the appropriate waste bottle. Add 10 ml. of hot 6 M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  to the resin and permit to pass through, catching the Mo eluate in a clean 40-ml. centrifuge tube (Note 6).
  4. To the eluate add 2 ml. of conc.  $\text{NH}_4\text{OH}$ , stir, and then add 10 drops of Fe carrier. Boil for 1 min. with stirring. Centrifuge.
  5. Add the supernate to an ice-cold mixture of 6 ml. of conc.  $\text{HNO}_3$ , and 1 ml. of  $\text{Br}_2\text{-H}_2\text{O}$ , and cool in an ice bath for about 5 min. Add 10 ml. of  $\alpha$ -benzoinoxime solution and stir vigorously. Filter onto No. 41 H Whatman filter paper, completing the transfer with 1 M  $\text{HNO}_3$ .
  6. Place the filter paper and contents in a porcelain crucible (Coors 0) and ignite to  $\text{MoO}_3$  at  $550^\circ$  for about  $3/4$  hr. (Note 7).
  7. After ignition allow the crucible to cool and grind the  $\text{MoO}_3$  to a fine consistency with the end of a stirring rod. Add 2 drops of ethanol and slurry; then add an additional 5 ml. of ethanol, stir, and filter onto a previously washed, dried and weighed No. 42 Whatman filter circle, using a ground-off Hirsch funnel and stainless steel filter chimney. Wash with ethanol and dry at  $110^\circ$  for about 10 min. Cool, weigh, and mount (Note 8).

NOTES

1. If the sample contains large amounts of U or  $\text{PO}_4^{=}$ , at this point precipitate the Mo with 10 ml. of  $\alpha$ -benzoinoxime solution. Stir well, centrifuge, and filter onto No. 41 H Whatman filter paper.

PROCEDURE B (Cont'd)

- Wash the precipitate well with 1 M  $\text{HNO}_3$ . (The filtrate and all washes are placed in the appropriate waste bottle.) Ignite the precipitate for about 15 min. at  $550^\circ$ . Dissolve the  $\text{MoO}_3$  with 3 drops of conc.  $\text{H}_2\text{SO}_4$  by heating to boiling. Dilute to 5 ml. with 6 M  $\text{HCl}$ , add 1 ml. of  $\text{Br}_2\text{-H}_2\text{O}$ , boil, and proceed to Step 2.
2. If it appears that exchange between carrier and radiomolybdenum might be incomplete, perhaps because of the presence of some organic compound, add 0.5 to 1.0 ml. of conc.  $\text{H}_2\text{SO}_4$  to sample and Mo carrier and evaporate the solution to dense white fumes. Cool and add 4 to 5 ml. of 6 M  $\text{HCl}$  and 1 ml. of  $\text{Br}_2\text{-H}_2\text{O}$ . Then proceed to Step 3. (Fuming with conc.  $\text{H}_2\text{SO}_4$  should also be carried out if the sample contains appreciable  $\text{NO}_3^-$  ion.)
  3. The anion resin, Dowex-1, is prepared for use in the following manner. Place a large quantity of the dry resin in a large tube (3 to 4" diameter and 1 to 1-1/2' long) with a medium or coarse fritted disk at the bottom. Slurry with methanol or ethanol while the bottom of the tube is stoppered and then suck the resin dry. Slurry the resin with conc.  $\text{HCl}$  containing about 1 ml. of 0.5 M  $\text{NaBrO}_3$  per 100 ml. of  $\text{HCl}$  and let the slurry stand for at least 30 min. (Anion resins, as obtained commercially, have reducing properties. The  $\text{NaBrO}_3$  presumably oxidizes any reducing species present in the resin.) Allow the resin to drain, and then repeat the treatment. Wash the resin with a large volume of distilled  $\text{H}_2\text{O}$ . The tube should be filled with  $\text{H}_2\text{O}$ , slurried, and sucked dry at least five times. Slurry the resin with a 1:1 mixture of  $\text{H}_2\text{O}$  and conc.  $\text{NH}_4\text{OH}$  and let stand for a while. Suck the resin dry and rinse with four to five fillings of distilled  $\text{H}_2\text{O}$ . Then slurry the resin with 6 M  $\text{HCl}$ , allow to stand, and suck dry. Slurry again with the acid and transfer the slurry to a storage bottle.

#### PROCEDURE B (Cont'd)

4. To prepare the anion column for use: (a) place a small plug of glass wool in the tip of the column; (b) add 4 to 5 cm. height of resin; (c) allow the acid to drain off.
5. The HF-HCl wash removes moderate quantities of U and Pu.
6. If the sample contains macro quantities of Pu, an additional column step should be performed. Add 3 ml. of conc.  $\text{HNO}_3$  to the Mo eluate and precipitate, ignite, and dissolve the Mo as in Note 1. Repeat Step 2, with the exception of the addition of 3 M  $\text{NH}_4\text{OH}$ . Elute Mo with  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  as in Step 3 and proceed to Step 4.
7. A stream of air flowing through the muffle furnace aids in the conversion of the Mo(VI)-benzoinoxime complex to  $\text{MoO}_3$ .
8. The samples can be mounted on Al plates with two-sided Scotch tape and covered with Mylar film. Four drops of Zapon solution (1 per cent Zapon in ethanol) are used to keep the  $\text{MoO}_3$  under the Mylar film.

#### PREPARATION AND STANDARDIZATION OF CARRIER

Dissolve 18.4 g. of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ , add 1 ml. of 0.5 M  $\text{NaBrO}_3$ , and dilute to 1 liter with 6 M  $\text{HCl}$ . Pipet 5.0 ml. of the solution into a 50-ml. beaker and dilute to about 20 ml. Add 1 ml. of  $\text{Br}_2\text{-H}_2\text{O}$ , 3 ml. of conc.  $\text{HNO}_3$ , and cool in an ice bath for 10 to 15 min. Add 15 ml. of  $\alpha$ -benzoinoxime solution, stir vigorously, and let stand for 5 min. Filter onto No. 42 Whatman filter paper, rinse the beaker with 1 M  $\text{HNO}_3$ , and transfer the rinsings to the filter paper. Transfer precipitate and paper to a weighed porcelain crucible (Coors 1) and ignite to the oxide at  $550^\circ$  for 1 hr. Cool and weigh the  $\text{MoO}_3$ .

## MOLYBDENUM

### PROCEDURE C

#### INTRODUCTION

This procedure for the radiochemical determination of Mo in fission product mixtures is based primarily on ether extractions and is derived from the procedure of Wiles and Coryell.<sup>59</sup> The main steps in the procedure are diethyl ether extraction of Mo from about 6 N HCl, removal of co-extracted impurities by ferric hydroxide precipitation, and precipitations of Mo with 8-hydroxyquinoline for chemical yield determination and counting. Precision of individual determinations is about 1 per cent (standard deviation) and purities are greater than 99 per cent. Chemical yields are about 60 per cent and 8 determinations can be made in about 8 hours.

#### PROCEDURE

1. To the sample in a 250-ml. separatory funnel add 1.0 ml. of Mo carrier solution, 1 ml. Te carrier solution (10 mg/ml), 2 mg.  $\text{Fe}^{+3}$ , a few drops 2.0 M  $\text{NaBrO}_3$  (Note 1), and adjust the total volume to 15-30 ml. and the acidity to 6 N in HCl.
2. Extract the solution with 100 ml. diethyl ether which has been equilibrated with 6 N HCl, and discard the aqueous layer (Note 2).
3. Wash the ether phase twice with 2 ml. 6 N HCl and discard the washings. Back extract the Mo with two 10-ml. portions of  $\text{H}_2\text{O}$ . Discard the ether layer.
4. Add  $\text{NH}_4\text{OH}$  to precipitate  $\text{Fe}(\text{OH})_3$  (Note 3). Centrifuge and discard the precipitate; add 1 mg.  $\text{Fe}^{+3}$  to the solution, stir, centrifuge and discard the precipitate.
5. Add 10 mg. Re holdback carrier and 1 drop methyl orange to the supernatant solution. Make the solution just acid with HCl. Add 5 ml. of 5 per cent  $\text{NaC}_2\text{H}_3\text{O}_2$ , heat nearly to boiling and precipitate the Mo by adding 1 ml. of 5 per cent 8-hydroxyquinoline in 1 N HCl (Note 4). Centrifuge, wash the precipitate

## PROCEDURE C (Cont'd)

with 15 ml.  $H_2O$ , transfer to a weighed filter disc, wash with 5 ml. ethyl alcohol and with 5 ml. diethyl ether, dry at  $120^{\circ}C$  for 15 min., cool in air for 20 min., weigh and mount for counting.

### NOTES

1. Addition of  $NaBrO_3$  is to ensure the presence of Mo in the extractable hexavalent state. However, if the previous history of the sample is such that exchange between carrier and radioactive atoms may be incomplete by this procedure, digestion with conc.  $HNO_3$  followed by destruction of the  $HNO_3$  with conc.  $HCl$  is necessary.
2. Fission product elements in addition to Mo which are extracted to varying degrees under these conditions are Ga, Tc, As, Ge, Te, Sn, Sb, I, Br.
3. The  $Fe(OH)_3$  precipitation serves to remove most of the contaminating elements extracted by the ether.
4. The precipitation of molybdenum 8-hydroxyquinolate provides additional decontamination from some of the elements extracted with Mo by diethyl ether, in addition to furnishing a suitable gravimetric and counting precipitate for Mo.

### PREPARATION AND STANDARDIZATION OF CARRIER

Dissolve 18.4 g  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  in 1 liter  $H_2O$ . Standardize the solution by withdrawing quadruplicate aliquots of 2.00 ml. and to each aliquot add 20 ml.  $H_2O$ . Make the solutions just acid to methyl orange, add 5 ml. 5 per cent  $NaC_2H_3O_2$ , heat nearly to boiling and add 2 ml. 5 per cent 8-hydroxyquinoline in 1  $N$   $HCl$ . Let stand several minutes and filter through a tared fine sintered glass crucible, wash precipitate with 15 ml.  $H_2O$ , 5 ml. ethyl alcohol, and 5 ml. diethyl ether. Dry precipitate at  $120^{\circ}C$  for 15 min., cool in air 20 min., weigh. Repeat drying process to constant weight.



## MOLYBDENUM

### PROCEDURE D

#### INTRODUCTION

This procedure for the radiochemical determination of Mo in fission product mixtures is based on ion exchange techniques which give quantitative recoveries of separated elements.<sup>78</sup> In addition, several other elements (Zr, Nb, Np, U, Te, Pu) are sequentially removed with quantitative recoveries. Direct gamma-ray counting of isolated solutions can be done in a well-type NaI(Tl) scintillation counter. Principal steps in the procedure are separation of Ru by volatilization with  $\text{HClO}_4$ , adsorption of Mo (and other indicated elements) on an anion exchange resin column from conc. HCl, elution of Zr with 12 N HCl-0.06 N HF, elution of Np, Nb and Pu with 6.0 N HCl-0.06 N HF (Note 4), elution of U and Te with 0.1 N HCl-0.06 N HF (Note 6), and elution of Mo and Tc with 12 N  $\text{HNO}_3$ . Precision of individual determinations is about 2 per cent (standard deviation), and purities are greater than 99 per cent. Chemical yields are 100 per cent, and about 12 determinations can be made in a day.

#### PROCEDURE

1. To a 1-5 ml. sample in a centrifuge tube (Note 1) add 1 ml. conc.  $\text{HClO}_4$ , 1 ml. conc.  $\text{HNO}_3$ , and 2 drops conc.  $\text{H}_2\text{SO}_4$ , heat to fumes of  $\text{H}_2\text{SO}_4$  (Note 2), let cool and carefully add about 2 ml. conc. HCl.
2. Quantitatively transfer the solution to a 0.2 cm<sup>2</sup> by 6 cm. high column of Dowex-2 anion exchange resin in the chloride form using washes of conc. HCl as required. Remove Zr quantitatively from the column by elution with 12 ml. 12 N HCl-0.06 N HF containing 2-3 drops of  $\text{Br}_2$  water (Note 3). A flow rate of 1 drop per 10 seconds is used here and in subsequent elution steps. Elute Np, Nb and Pu quantitatively with 12 ml. 6.0

PROCEDURE D (Cont'd)

N HCl-0.06 N HF containing 2-3 drops of conc.  $\text{HNO}_3$  (Notes 3 and 4).

3. Dry the column by allowing air to pass through it and then washing it with 3-4 ml. ethyl alcohol (Note 5). After the alcohol has drained through, remove U and Te quantitatively by elution with 12 ml. 0.1 N HCl-0.06 N HF (Note 6).
4. Elute Mo and Tc quantitatively from the column in 12 ml. 12 N  $\text{HNO}_3$ . Count the eluate directly in a well-type NaI (Tl) scintillation counter (Note 7).

NOTES

1. Since recoveries are quantitative by this procedure, addition of carriers is not necessary.
2. Distillation with  $\text{HClO}_4$  serves to remove Ru which is otherwise likely to contaminate Zr and other fractions in an irreproducible way. If recovery of Ru is desired the distillation can be performed in a distillation apparatus made from a 30-40 ml. test tube with an air inlet tube reaching nearly to the bottom of the test tube. A side arm delivery tube is exhausted into a Ru collecting solution of 2-3 N NaOH. The distillation is performed with an air stream passing through the system.
3. The eluant contains an oxidizing agent to keep Mo and U in their highest oxidation states.
4. If either Np or Nb-Pu fractions free of the other are desired, a two-step elution can be performed at this point. Following removal of Zr, the Np can be quantitatively eluted with 12 ml. 6.5 N HCl-0.004 N HF. Then the Nb and Pu can be quantitatively eluted together with 12 ml. 6.0 N HCl-0.06 N HF.

PROCEDURE D (Cont'd)

5. The resin must be dried before elution of U and Te or some Mo will be lost in that fraction due to the minimum in the Mo  $K_d$  curve at about 2 N HCl.
6. If isolation of separate Te and U fractions is desired, a two-step elution can be performed at this point.<sup>104</sup> Following removal of the Nb fraction the column is washed with 3-5 ml. of absolute alcohol made 1 N in phosphoric acid. Te is quantitatively eluted with 25 ml. 1 N  $H_3PO_4$ . The resin is converted back to the chloride form with 3-5 ml. of absolute alcohol saturated with HCl gas. Then U is quantitatively eluted with 12 ml. 0.1 N HCl-0.06 N HF.
7. Gamma-ray counting is done in a 3" diameter by 3" high NaI(Tl) crystal with a well about 1-1/8" diameter by 2-1/4" deep. With such a crystal, counting efficiencies are insensitive to volume differences of 2-3 ml.



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