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CHEMICAL ANALYSIS OF ALKALI METAL TUNGSTEN BRONZES

by

Bruce Alan Raby

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In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

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Of Science and Technology
Ames, Iowa

1963

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DEDICATION

This thesis is dedicated to my
parents and my wife. Their support,
encouragement, help, and sacrifices
made my graduate education a reality
and smoothed the course over which
I have recently passed.

I. THE ALKALI METAL TUNGSTEN BRONZES

A. Introduction to the Tungsten Bronzes

In 1823 Wöhler discovered the unique materials which are now known as sodium tungsten bronzes (144). Bronzes of several other metals have been prepared and characterized in the years since his discovery. The term "bronze" is apparently derived from the metallic luster and conductivity of the materials. In fact, some of the bronzes are used as metallic pigments.

It is generally believed that the tungsten bronzes are non-stoichiometric compounds having a nominal composition M_xWO_3, which also may be expressed as $M_xW(V)_xW(VI)_{1-x}O_3$. Some workers think that the oxygen-to-tungsten ratio is actually less than three. Bronzes are known in which the metal "M" is: hydrogen, lithium, sodium, potassium, rubidium, cesium, mixed sodium and potassium; copper, silver; barium; aluminum, thallium, scandium, yttrium; titanium, zirconium, hafnium, thorium; lead, uranium, or nickel. Tungsten may be replaced by molybdenum, titanium, vanadium, niobium, or tantalum. An analogous material appears to exist in the sodium-aluminum-fluoride system.

The most familiar bronzes crystallize in some modification of that cubic system known as perovskite (78, 79, 99). However, tetragonal and hexagonal crystal systems are recognized for certain composition ranges of the bronzes.

Several good, general references, which provide more detailed discussions of the bronzes and their properties, are available (37, 98, 99). Preparative methods are reviewed in these references.

Chemists and physicists have been interested in the chemical and physical properties of the tungsten bronzes for many years. The following items are commonly mentioned in discussions concerning the tungsten bronzes: their uses as catalysts and thermocouples, conductivity and resistivity, color, crystal structure, density, electrode behavior, electronic specific heat, electrostatic energy, Hall and Seebeck coefficients, magnetic properties, thermal properties, general chemical behavior, and preparation.

Because all these properties depend on the composition of a bronze, it is necessary to have good analytical methods for the determination of the constituents in order that composition-property correlations can be made. The chemical literature contains no reports of attempts to effect a total constituent analysis for any bronze. Consequently, one is tempted to question earlier values for the alkali metal-to-tungsten and the oxygen-to-tungsten ratios. Furthermore, a convenient and effective dissolution/decomposition procedure has not yet been developed for the bronzes. The research reported in this thesis evolved from a need to analyze specimens of tungsten bronzes and from the subsidiary need to develop a better analytical determination of tungsten. This work is restricted to the alkali metal tungsten bronzes and to tungsten trioxide. The latter compound is interesting because of its uses as a standard tungsten compound and as a gravimetric weighing form.

B. Prior Analytical Chemistry of the Alkali Metal Tungsten Bronzes

The interest in the composition and properties of the bronzes has led to studies directed toward the analysis of these materials, either partially or indirectly *in toto*. Three publications discuss general approaches to the analysis of bronzes (77; 127; 139, pp. 234-6). In order to understand why this new study was undertaken, the earlier analytical methods must be reviewed briefly and their shortcomings discussed. A ubiquitous problem is the lack of standard bronzes to serve as referee materials for composition determinations.

1. Decomposition and dissolution methods

Alkali metal tungsten bronzes are quite inert to attack by chemical reagents unless the reagents are potent or the reaction conditions are vigorous. This chemical inertness causes inconveniences in analytical procedures and, in some cases, produces strong disadvantages. There are two principal types of attack which have been employed to decompose the bronzes: solution in fused salts, and treatment with hot gases.

Solution in fused salts can be accomplished either by acidic or basic oxidation. Acidic oxidizing conditions are produced in melts of ammonium peroxydisulfate (77) or mixtures of ammonium sulfate and concentrated sulfuric acid (17). Either acidic attack is slow and requires many hours, or even a few days, for complete decomposition and dissolution of the sample. Furthermore, ammonium compounds tend to spatter badly and such fusions can result in the loss of significant amounts of material.

Basic melts are composed of mixtures containing an oxidant (an alkali metal peroxide or nitrate) and a base (an alkali metal hydroxide or carbonate) (12, 121). Although basic fusions dissolve the bronzes with great ease and rapidity, they do swamp the alkali metal of the bronze with a large amount of the same or of another alkali metal and thus render a determination more difficult.

Quite different approaches to sample decomposition are derived from the reaction of certain hot gases with the bronzes: oxidation by oxygen, chlorination, and reduction by hydrogen. Treatment of alkali metal tungsten bronzes with oxygen between 500°C and 1000°C yields a mixture of alkali metal tungstate and tungsten trioxide (12, 77, 127). However, alkali metal tungstates melt at relatively low temperatures and have a pronounced tendency to wet the container and creep out of it. Consequently, some loss of material occurs with this method.

The chlorination technique employs hydrogen chloride gas or hydrogen chloride-oxygen mixtures (24, 76, 78, 92, 126, 127). Hydrogen chloride-chlorine mixtures, chlorine, and nitrosyl chloride have been used at this laboratory for the same purpose (106). Bronzes will react with these gases to yield a mixture of tungstenyl chloride, WO_2Cl_2, oxygen or water, and alkali metal chloride. A difficult problem is caused by the volatility of the alkali chlorides and by the slowness of the reaction.

Hydrogen reduction of bronzes produces a mixture of water, tungsten metal, and alkali metal oxide (24, 127). This is a useful method for the determination of tungsten, especially in tungsten trioxide. In this laboratory, it is the method of choice for the determination of tungsten. A detailed discussion of hydrogen reductions is given in Chapter V.

2. Determination of the alkali metal

Analysts have used an interesting variety of schemes for the determination of the alkali metal constituent in tungsten bronzes. These schemes divide into three broad categories: wet chemical methods, dry chemical methods, and physical methods. Some of the methods are applied after the decomposition of the bronzes and some are the direct result of decomposition procedures.

Wet chemical analyses must necessarily follow one of the decomposition procedures. The alkali metal can be precipitated and weighed in a form such as sodium zinc uranyl acetate (17). Any of the alkali metals can be determined gravimetrically as the sulfate (18). One should understand that these methods probably cannot be applied if a fusion has been employed to decompose the sample.

If an alkali metal chloride is one of the decomposition products, one can precipitate or titrate the chloride with silver (18).

There are two principal dry chemical methods. Both result directly from reactions of bronzes with hot gases. One product of the chlorination procedure is an alkali metal chloride. It was thought that this product could be weighed directly because tungstenyl chloride is volatile and will distill out of the sample boat (76, 77, 127). However, the alkali metal chloride is too volatile and the reaction is too slow for the method to be practical.

In the case of oxidation by oxygen, the sample exhibits a weight increase. The amount of oxygen taken up by the bronze is proportional to the amount of tungsten(V) in the material and, hence, is also proportional to the amount of alkali metal present. From the weights before and after oxidation, and with the assumption that the oxygen-to-tungsten ratio is 3.000, one can calculate the x-value for the alkali metal. Although it has been argued that the oxygen-to-tungsten ratio is exactly three (37, 78, 79), this point should be proved by direct determination of the oxygen content in bronzes. Furthermore, the method has limited usefulness, because it does not determine the alkali metal directly.

Physical determinations of the alkali metal content include both destructive and non-destructive methods. One non-destructive analysis for alkali metals is the x-ray method of Brown and Banks (18). So far, it has been possible to apply this method to cubic bronzes only. A further difficulty is that the calibration of the technique depends upon some other kind of analysis to establish the correlation between composition of the bronze and its lattice parameters. Another non-destructive method of analysis is the neutron activation method developed by Reuland (106).

There are two destructive analytical methods for the alkali metals. One is based on the flame photometric determination of the alkali metal content of the decomposition products (31). The other is the direct spectrographic determination of lithium and sodium (143).

3. Determination of the oxygen

This has been a difficult problem to solve and it is an especially important one because it is necessary to determine oxygen directly in order to establish accurately the oxygen-to-tungsten ratio in the bronzes. Oxygen can be estimated if the alkali metal and tungsten contents are known with good accuracy. It must be assumed, of course, that the alkali metal, tungsten, and oxygen are the only constituents of the bronze. Any errors occuring in the determinations of alkali metal and tungsten could be compounded in the estimation of oxygen by difference.

Attempts have been made to reduce a bronze with hydrogen and to trap and weigh the water evolved by the reaction (24, 127). Unfortunately, though, the alkali metal retains part of the oxygen and the method leads to low results unless the amounts of alkali metal and tungsten are also known.

4. Determination of the tungsten

The determination of tungsten is a really unsatisfactory part of analyzing the alkali metal tungsten bronzes. All methods so far applied to the determination of tungsten have been gravimetric. Tungsten has been converted to tungstate, which was then precipitated by tannin-cinchonine (12, 31), cinchonine alone (17), cinchonine-nitric acid (32), nitric acid (18, 121, 122), mercury(I) (77), or mercury(II) (127). In each case the precipitate was ignited to tungsten trioxide. These methods are subject to criticism because there is real doubt about the completeness of the precipitations and about the conditions for ignition to the oxide.

The problems encountered in the chemistry of tungsten have prompted a special study of the analytical chemistry of the element. Chapter V considers the analytical chemistry of tungsten in more detail.

II. APPLICATION OF BROMINE TRIFLUORIDE TO THE ANALYSIS OF ALKALI METAL TUNGSTEN BRONZES

A. Properties of Bromine Trifluoride

The history of and the preparative methods for bromine trifluoride are too well known to require review in this thesis. Several excellent review articles thoroughly discuss this compound (15, 16, 46, 61). This section will discuss only those particular properties of bromine trifluoride which are especially pertinent to the work being described.

1. The bromine-fluorine system

Commercial bromine trifluoride contains up to 15 mole per cent of bromine pentafluoride and some bromine (69, 81). One of the products which form when bromine trifluoride or bromine pentafluoride decomposes is bromine and that element will certainly be present in reaction product mixtures. Bromine monofluoride is an unstable intermediate in the preparation of bromine trifluoride from bromine and fluorine. It also results from the reaction of bromine with bromine trifluoride (51). Consequently, one must assume that any of these materials may be present with bromine trifluoride.

Studies have investigated the possibility of separating bromine trifluoride from bromine pentafluoride by distillation (75, 81, 86, 146). Similar investigations were made for the separation of bromine from bromine trifluoride (51, 86, 145) and from bromine pentafluoride (86, 145). In both of the latter cases, azeotropes were found; therefore, one cannot expect to completely purify bromine trifluoride by distillation. However, bromine does not interfere with the use of bromine trifluoride as a reagent in the analysis of alkali metal tungsten bronzes. Table 1 presents some useful physical data for compounds of the bromine-fluorine system (15, 64, 75, 110, 111, 112).

Table 1. Physical properties of the bromine-fluorine system

Compound	Melting point (°C)	Boiling point (°C)	Thermal stability (°C)
Bromine	-7.3	58.8	
Bromine monofluoride	-33	20	<50
Bromine trifluoride	8.8	127	170-180
Bromine pentafluoride	-61	41	>400

2. Solvent properties

Bromine trifluoride is a pale yellow material in both the liquid and solid states. The liquid is an inorganic, proton-free, ionizing solvent (61). Its volatility, Trouton constant, dielectric constant, and conductivity indicate that it is associated and has ionizing ability. Because it is an ionizing solvent, bromine trifluoride has a definite acid-base system and other water-like properties (46, 61). These are the properties which make the compound such an interesting and useful chemical. Chapter V discusses an attempt to determine tungsten by making use of this non-aqueous acid-base system.

All the alkali metals, with the possible exception of lithium, are sufficiently soluble in bromine trifluoride solution to avoid complications due to incomplete solution (61, 96, 97, 117). Table 2 gives some data for the solubility of alkali metal fluorides, probably as alkali metal tetrafluorobromates(III), in bromine trifluoride solutions. Not much is known about the solution behavior of tungsten

Table 2. Solubilities of alkali metal fluorides in bromine trifluoride and in water

Alkali metal fluoride	Solubility[a] in BrF_3	Solubility[a] in H_2O
Li	0.125	0.27
Na	0.75-2.08	4
K	4.73-5.10	92.3
Rb		130
Cs	18.8-24.0	366

[a] Solubility in gm/100 gm solvent.

hexafluoride in bromine trifluoride, but this is probably not important because the hexafluoride is a gas at room temperature.

3. Reactions with oxygen-containing materials

Bromine trifluoride readily reacts with many oxygen-containing materials. These reactions produce both fluorides and oxyfluorides, and many of the reactions apparently liberate the combined oxygen quantitatively as elemental oxygen. It has been possible to apply this property of bromine trifluoride to the preparation of unusual fluorides and to the analysis of oxygen in various materials.

Studies show that many oxides and oxy-salts react quantitatively with bromine trifluoride (61, 93, 100, 119). These papers contain data about reaction times, reaction temperatures, and completeness of the reactions. Bromine trifluoride has been used to determine oxygen in titanium and its alloys (38, 94), and in uranium and uranium hydride (67). Potassium tetrafluorobromate(III), $KBrF_4$, has beem employed for the determination of oxygen in fluoride salts (59), in yttrium and its salts (4), and for other materials (3, 5, 6, 58). Oxygen in organic compounds has been determined with difluorobromine(III) hexafluoroantimonate(V), BrF_2SbF_6 (118). It is of especial interest to this research that tungsten-oxygen compounds react quantitatively with bromine trifluoride to yield oxygen and the volatile tungsten hexafluoride (65, 94). E. Banks and his coworkers have considered the use of bromine trifluoride to determine oxygen in the alkali metal tungsten bronzes (7).

4. Construction materials

Because bromine trifluoride is such a reactive chemical, there are relatively few materials which can be used for fabricating containment vessels and handling apparatus. An appreciable body of research has been performed with this compound and a major portion of the research has been specifically directed toward studies of its corrosive activities (115, 128, 129). Fortunately, if one is careful about controlling moisture and temperature, there is a sufficient variety of construction materials available which are able to resist or deny corrosion by bromine trifluoride.

The most widely employed construction materials are nickel (62, 69, 104, 119, 128, 129, 130, 134) for temperatures below 750°C and its alloys such as Inconel (128, 129) and Monel (69, 128, 129, 130, 134). If the temperature is kept below 400°C, copper is recommended. Aluminum has been used successfully (129, 130, 145). Silica (48), quartz (27), Vycor (86, 145), and Pyrex (48) resist etching if the system is perfectly anhydrous. Gaskets are fabricated from Teflon (119, 128, 129, 130, 134), Kel-F (134), and Fluorothene (62, 130). Silver solder is preferred for assembly (130). Most workers have used the Hoke brand of valves: the 480 series barrel type with phosphor bronze bellows and Kel-F pads; or the 410 series diaphragm type with an Inconel diaphragm (62, 69, 119, 130). Various alloys of iron (129) and cobalt have been useful. Platinum (116) and sapphire (134) can be employed for some applications. If the solubility of metal fluoride in bromine trifluoride is a significant criterion, then nickel, zirconium, iron, copper, aluminum, cobalt, and chromium are logical candidates for construction materials (61, 96, 97, 117).

Other workers have found that some of these same materials are not so satisfactory. Silver solder sometimes introduces the very soluble silver fluoride into bromine trifluoride solutions (104). Platinum can be dissolved, especially in bromine-rich solutions of the reagent (100, 104, 128, 129). Glass and quartz may be severely etched (129). One author claims that nickel cannot be used if it is necessary to prevent the decomposition of bromine trifluoride into bromine and/or bromine monofluoride (27). It has been our experience in this laboratory that copper will completely dissolve if it is left in contact with liquid bromine trifluoride for about six weeks.

5. Safety precautions

Bromine trifluoride is a dangerous chemical unless it is properly handled. It will affect human skin by producing hyperemia, swelling, ulceration, necrosis, and vesication

(63). Its reactions with many common organic and inorganic materials are violent or explosive (15, 109, 119). Special emphasis should be placed on the fact that bromine trifluoride must be kept away from water (15, 109).

Advice is available for obtaining maximum safety while working with bromine trifluoride (49, 75, 133). These references contain information about clothing, ventilation, first aid, waste disposal, and safety equipment. They also warn against working alone and recommend the "buddy" system when this reagent is being handled or used.

B. Properties of Tungsten Hexafluoride

There are two fine review articles which discuss the preparation, properties, and history of tungsten hexafluoride (20, 45). Only its pertinent properties will be reviewed in this section.

1. The tungsten-fluorine-oxygen system

In addition to tungsten hexafluoride, WF_6, there are possibly two other compounds which might be formed by the fluorination of oxygen-containing tungsten compounds (20, 45). One of these is tungstenyl fluoride, WO_2F_2. It is not definitely known whether this compound actually exists; certainly, nothing is known of its properties. Therefore, it was not considered in connection with this work.

Tungsten oxytetrafluoride, WOF_4, is the direct product or is a by-product of a number of reactions. It is a solid at room temperature and can be separated from the hexafluoride by distillation. It has been observed in the course of this work that the compound does not form in the presence of excess bromine trifluoride. There is some evidence that it will form from tungsten hexafluoride in the presence of a small amount of water vapor or a large amount of oxygen.

The useful physical properties of these compounds are given in Table 3 (21).

Table 3. Physical properties of the tungsten-fluorine-oxygen system

Compound	Formula	Melting point (°C)	Boiling point (°C)
Tungstenyl fluoride	WO_2F_2	?	?
Tungsten oxytetrafluoride	WOF_4	105	186
Tungsten hexafluoride	WF_6	2	17.1

2. Chemical properties

Tungsten hexafluoride readily reacts with water to form precipitates of $WO_3 \cdot nH_2O$ (113). It is quite soluble in alkaline aqueous solutions of potassium hydroxide, ammonia, etc., to form solutions of orthotungstate, $WO_4^{=}$ (108, 113). This work indicates that both the hexafluoride and the oxytetrafluoride yield the oxide when exposed to moist air or water.

It has been reported that tungsten hexafluoride will dissolve in bromine trifluoride to form a true solution. Apparently, not much is known about the behavior of the tungsten compound in this solvent system. Gutmann reports that the hexafluoride does not react with the solvent to produce an acidic solution (60). However, Clark states that the solution is weakly acid (29). It has been observed for potassium, rubidium, and cesium that the following reaction occurs (30, 33):

$$M_2WF_8 + 2\ BrF_3 \longrightarrow WF_6 + 2\ MBrF_4 \qquad (1)$$

Reuland finds that the separation of tungsten and sodium is completely accomplished by distillation of a like solution (106).

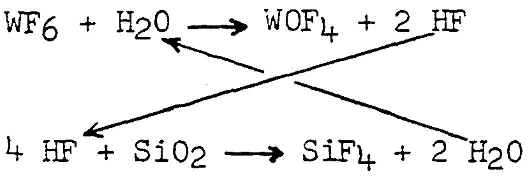
One can assume two things from the above information. First, it is necessary to handle the hexafluoride under strictly anhydrous conditions. Secondly, it is possible to distill tungsten hexafluoride out of strongly basic bromine trifluoride solutions. These considerations will be important in the last two sections of this chapter, wherein the analytical method for the tungsten bronzes will be proposed.

3. Construction materials

Because tungsten hexafluoride is a less reactive compound than the halogen fluorides, it is easier to find corrosion resistant materials for the construction of handling systems. In general, the same construction materials are used for the tungsten fluorides and oxyfluorides as are used for the halogen fluorides.

Nickel and Monel are popular metals (8, 88). If the interior of the system is rigorously anhydrous, both glass (113) and Pyrex (21) are widely employed. The compound will not react with fluorocarbon greases (21, 56). Other inert materials are platinum, gold, copper, and Teflon (88, 113). Iron, zinc, tin, cobalt, lead, antimony, mercury, nickel, and copper are not attacked under anhydrous conditions, but they are corroded by moist tungsten hexafluoride and moist or warm tungsten oxytetrafluoride (113).

The presence of arsenic trifluoride will cause the hexafluoride to react with glass to form the oxytetrafluoride (113). The hexafluoride will corrode mercury seals (56). Moisture causes a cyclic reaction of tungsten hexafluoride with glass (88):



$$WF_6 + H_2O \longrightarrow WOF_4 + 2\ HF \qquad (2)$$

$$4\ HF + SiO_2 \longrightarrow SiF_4 + 2\ H_2O \qquad (3)$$

4. Safety precautions

Tungsten hexafluoride presents the usual hazards of a reactive compound (113). Because some of the lower oxidation states of tungsten, as well as the free metal itself, are relatively stable, the compound is an oxidant and a fluorinator. It reacts violently with water and ammonia. There is a question whether it oxidizes (102) or does not oxidize (101) organic materials like benzene.

Tungsten hexafluoride is a gas at room temperature and must be handled as such, with provisions being made for leakless containment and pressure excursions. When the compound is melted or frozen, there is a large volume change which must be considered in the volume design of containment vessels (136).

In general, it would be well to handle the tungsten hexafluoride with the same cautions that are employed with bromine trifluoride.

C. Vapor Pressure Data

Proposals for the purification of bromine trifluoride and for the separation of constituents must take into account the vapor pressures of various volatile compounds which occur in the system. Therefore, a graph of these important data (8, 20, 21, 45, 46, 51, 64, 75, 81, 88, 108, 110, 111, 112, 130) is presented in Figure 1.

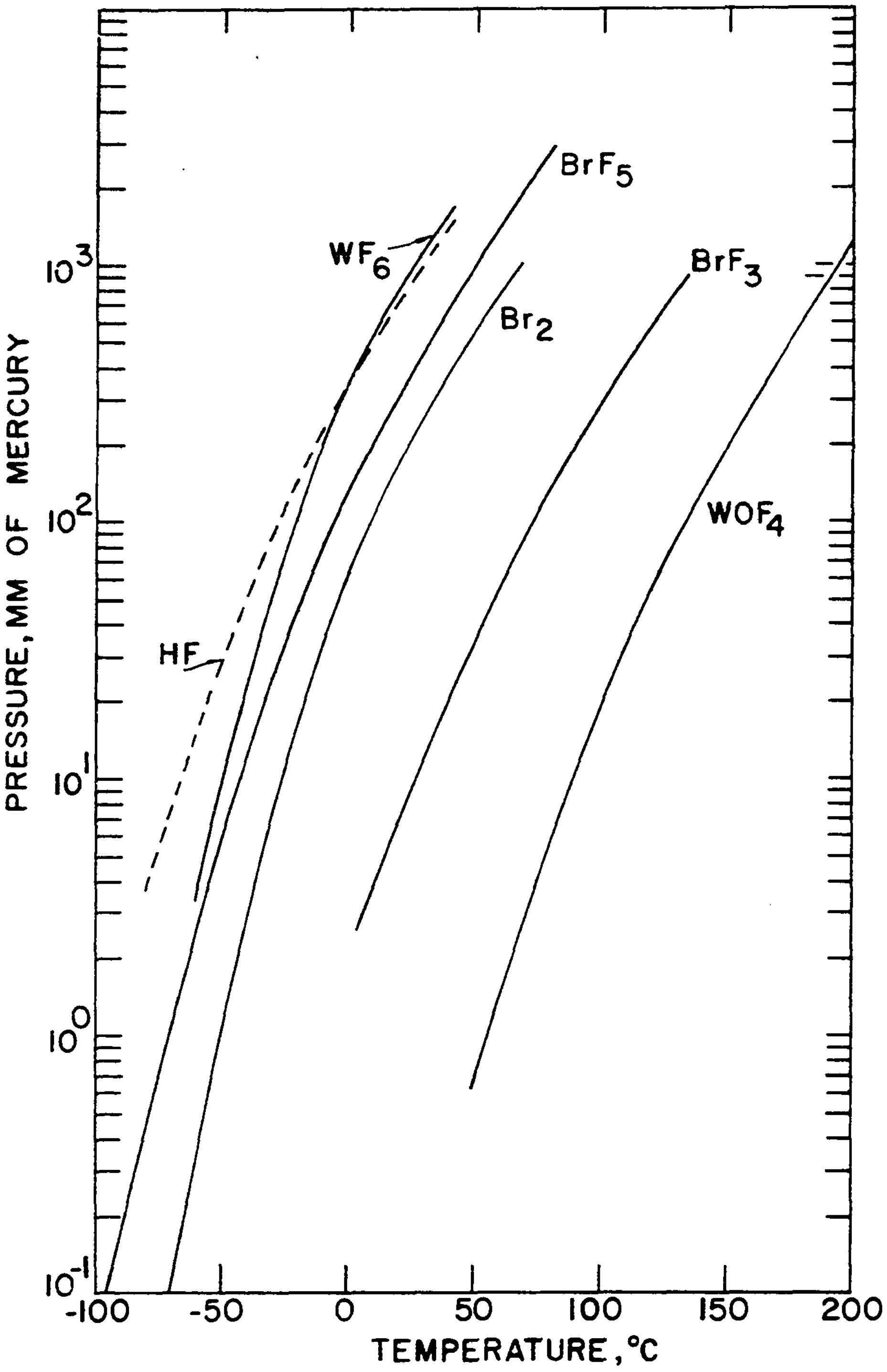


Figure 1. Vapor pressure curves of some fluorine compounds

D. Proposed Scheme for the Analysis of Alkali Metal Tungsten Bronzes

The following scheme for the analysis of the bronzes has been derived from the information given in the first three sections of this chapter. This scheme allows one to decompose the bronze, separate the constituents, and to determine the alkali metal and the oxygen. However, it was discovered that tungsten could not be approached within this scheme. The methods which were actually used for the determination of tungsten are discussed in Chapter V.

1. Decomposition of the sample

It is thought that an alkali metal tungsten bronze reacts with bromine trifluoride according to the equation:

$$M_xWO_y + (\frac{4x}{3} + 2)\ BrF_3 \longrightarrow$$
$$x\ MBrF_4 + y/2\ O_2 + WF_6 + (\frac{x}{6} + 1)\ Br_2 \qquad (4)$$

Although no direct attempt was made to prove that this is the correct reaction, several observations have been made during the course of the work which support the correctness of the postulated reaction.

First, manipulation of the products in the manner indicated by their assumed character leads to the correct results. Second, bromine is observed in the reaction mixture. Third, the stoichiometric amount of oxygen is produced.

Fourth, tungsten occurs in a colorless, gaseous compound which will form the solid, white oxytetrafluoride in the presence of moisture traces and will form tungsten trioxide hydrate when exposed to enough water. Fifth, and finally, the white product remaining in the reactor after all gases and liquids have been distilled away will react with dilute sulfuric acid to produce bromine, hydrofluoric acid, and alkali metal sulfate.

It has been further observed that lithium fluoride is not very soluble in bromine trifluoride and that the other alkali metal fluorides are quite soluble. These observations agree with the data given in Section A.2 of this chapter. Bromine is also quite soluble in the reagent (51, 104), a fact which was confirmed by this work. Experience here shows that tungsten hexafluoride is not appreciably soluble in bromine trifluoride; this observation is supported by Brasted (16).

2. Separation of the constituents

Because the four products and the excess bromine trifluoride have such a convenient separation of boiling points, it is quite feasible to fractionate the reaction mixture by distillation. It is necessary to separate the mixture into three groups: oxygen; alkali metal tetrafluorobromate(III); and a mixture of bromine, bromine trifluoride, and tungsten hexafluoride.

3. Determination of the constituents

The alkali metal is determined by treating the tetrafluorobromate(III) with dilute sulfuric acid and fuming to form the alkali metal sulfate. The determination is concluded gravimetrically. The details of the method are given in Chapter III.

Oxygen is determined manometrically. This method is described in Chapter IV.

All aqueous solutions of tungsten which also contain fluoride are rather complex in their behavior. Consequently, no method was developed out of this work for utilizing the tungsten hexafluoride formed by the decomposition of the bronze. It might have been possible to construct an appropriate pressure measuring device for the determination of tungsten as the hexafluoride (21, 34, 131), but this was deemed rather difficult.[1] A review of the various attempts to determine tungsten, as well as discussions of standard tungsten compounds and the analytical methods finally adopted, is given in Chapter V.

E. The Fluorination Apparatus

This is a general description of the fluorination apparatus and its operation. The whole system, except for the measuring manometer, is clamped to a sturdy steel rack

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[1] Hargreaves, G. B. Imperial Chemical Industries, Billingham, England. Construction of glass diaphragm pressure gauges. Private communication. 1962.

and is set into a six-foot hood so that the volatile fluorine compounds will not contaminate the laboratory atmosphere. The special equipment used for tungsten is described in Chapter V.

1. Construction materials

All tubing in the apparatus is copper, nickel or Teflon. Copper is cheaper and easier to obtain, therefore, it is the primary tubing material. Nickel is used for the inlets and outlets of all still pots and traps. A flexible Teflon tube connects the storage cylinder to the reagent still. All tubing connections are either silver soldered or Swage-lok Monel fittings. The still pot and trap flanges are Inconel, nickel, or copper. Glass is employed for the oxygen measuring subsystem and for the diffusion pump and its traps. Glass stop cocks are lubricated with Hooker's Fluorolube GR-362. The traps and still pots are constructed of Kel-F. The valves which are exposed to corrosive service are Hoke 410 series or 480 series valves.

2. Reagent purification subsystem

Commercial bromine trifluoride is available from Harshaw in mild steel cylinders which contain one or five pounds of the reagent. Vacuum distillation of the reagent from the cylinder into the reagent still frees the reagent from metal fluorides which have been formed from the cylinder walls. The reagent still column is a nickel tube packed with

Podbielniak No. 3018 nickel Heli-Pak and it is wrapped with a heating tape. An Inconel flange connects the Kel-F still pot to the column.

A second vacuum distillation separates the volatile impurities into a storage trap. This trap, like the reagent still pot, is made from a Kel-F test tube; the flange is copper. The storage trap contains thin nickel baffles. The volatile impurities removed by distillation are oxygen, nitrogen, bromine, bromine pentafluoride, and hydrogen fluoride.

3. Reactor vessel subsystem

The purified reagent is vacuum distilled into a second still pot which is exactly like the first. There is an alternate still pot made of Inconel which is sealed to the flange with Fluorothene gaskets or Monel "O" rings (Advanced Products Co.). The Inconel pot is used when higher temperatures or pressures are needed. This second still contains the sample. About ten milliliters of reagent are used with 0.2 to 0.5 gram of sample so that there will be a large excess of reagent to prevent the formation of tungsten oxytetrafluoride. The packed and heated column of this still is exactly like the reagent still column, except that it is about twice as long. After the reaction is completed, the still is packed in dry ice-acetone and the oxygen is pumped into the oxygen measurement subsystem. Then the remaining volatile compounds are vacuum distilled into the reagent still; the alkali metal tetrafluorobromate(III) remains in the still pot. The volatiles which were returned to the reagent still are vacuum distilled so the unused bromine trifluoride is available for other samples.

With the exception of the oxygen pump-out operation, all trapping of volatiles is done with liquid nitrogen traps. A still-pot heater is also used. It is a cylinder of wire gauze which will fit the still pot and it is wrapped with a heating tape.

4. Oxygen measurement subsystem

This subsystem is constructed entirely of Pyrex glass. There is a Töpler pump to transfer the oxygen from the reactor still into a constant volume manometer. There are three bulbs for containing the gas; they are approximately 250, 500, and 1000 milliliters in volume and can be used in various combinations to accommodate a wide range of sample sizes and oxygen contents. A pressure transfer manometer and a measuring manometer complete this subsystem. The measuring manometer contains King No. 200 indicating liquid, which has a density of 2.0 and is, therefore, about 6.5 times more sensitive to pressure changes than mercury.

5. Vacuum manifold subsystem

This subsystem includes a diffusion pump, a fore-pump, and a vacuum gauge. The diffusion pump probably is not necessary; the apparatus is usually operated on the diffusion pump bypass. The fore-pump is a rotary, mechanical pump. The vacuum gauge is a cold cathode gauge and is used to monitor the pressure during pump-out of the containment bulbs and the manometers. The valves in this subsystem are Imperial Teflon diaphragm valves. The manifold, except for the diffusion pump branch, is constructed of hard copper which is soft soldered and covered with two coats of Glyptal. Leak testing throughout the whole apparatus was accomplished by the use of a helium leak detector, blowing bubbles with a high internal pressure of helium, a Tesla coil, acetone and the vacuum gauge, and static leak tests.

Figure 2 shows a schematic diagram of the fluorination apparatus.

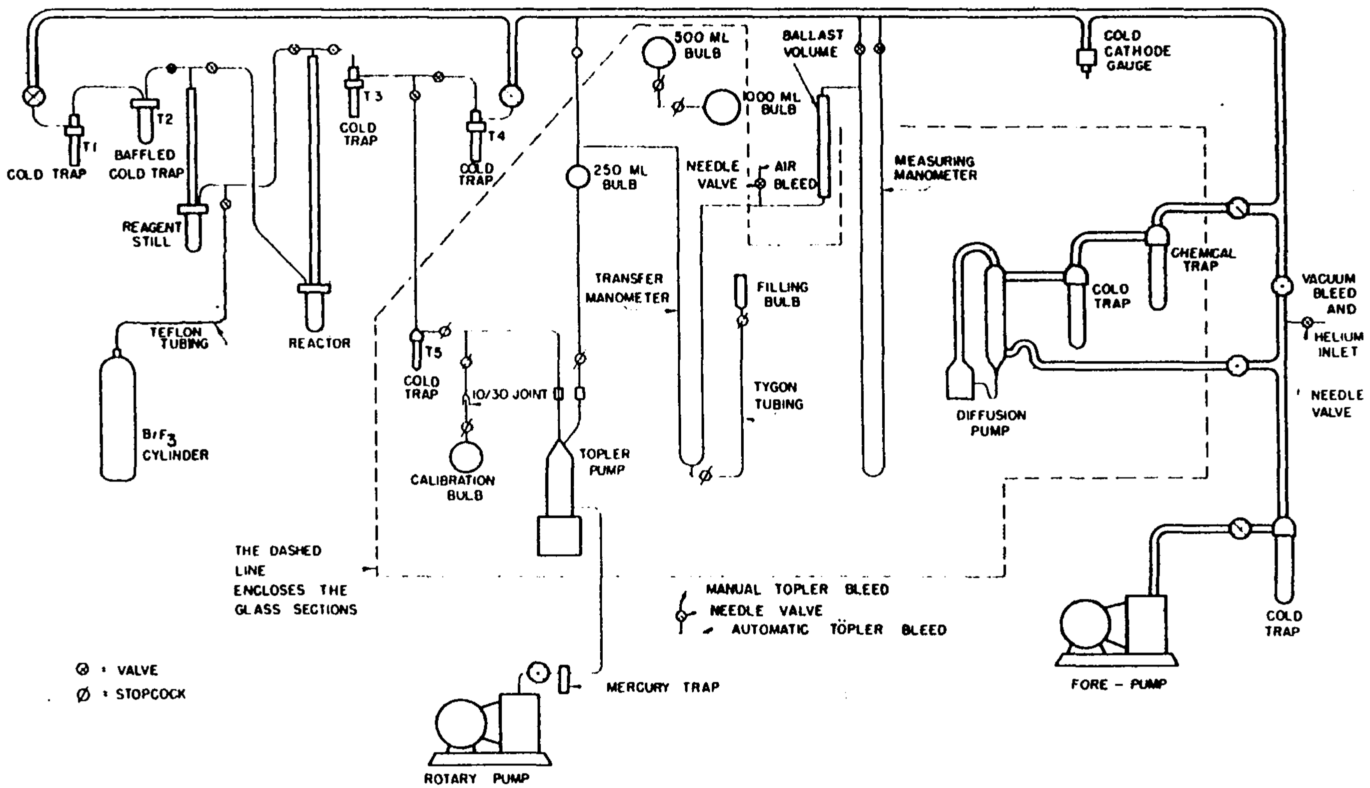

Figure 2. Schematic diagram of the fluorination apparatus

III. DETERMINATION OF THE ALKALI METAL

A. Determination of Lithium with Thoron

Thoron, 1-(2-arsonophenylazo)-2-hydroxynaphthalene-3,6,-disulfonic acid, has been used for the determination of lithium (137). This spectrophotometric method was tried as an approach to the determination of lithium in lithium tungsten bronzes after chlorination. However, the absorbancy-weight plot is not linear above 100 micrograms of lithium and this upper limit is too low for the demands of this problem. Furthermore, a method for all the alkali metals was needed; this method is restricted to lithium. Finally, chlorination did not prove to be a useful attack upon the bronzes.

B. Determination of Lithium and Sodium by Chlorination

The chlorination of tungsten bronzes (76, 77, 127) appeared to be a good method for the determination of alkali metals, because both tungsten and oxygen volatilize and the easily measurable alkali metal chloride remains in the reaction boat. A few experiments showed that the alkali metal chlorides are also volatile, a fact which is confirmed by Reuland (106). There seemed to be no obvious relationship between the volatilization rate of an alkali metal chloride and the compound from which it is derived or the composition of the chlorination atmosphere. It was not possible, therefore, to calculate the amount of alkali metal chloride from any features of curves like Figure 3. Table 4 presents a summary of results from chlorination experiments.

Table 4. Summary of chlorination experiments

Atmosphere	Substrate	Temperature (°C)	Hours	Results
NOCl	LiCl	500	2	5-8% loss
NOCl	LiCl	500	4	80% loss
NOCl	LiCl	810	1 1/2	75% loss
Cl_2	NaCl	650		1 1/2%/hr loss
Cl_2	Li bronze	770	1/2	rn complete[a]
Cl_2	Na bronze	650	7	rn complete[a]
$HCl-O_2$	LiCl	520	1 1/4	5% loss
$HCl-O_2$	Na bronze	600	12	rn complete[a]
$HCl-Cl_2$	Na bronze	650	2	rn complete[a]

[a] Volatilization of WO_2Cl_2 complete. Volatilization of MCl continues beyond this point.

C. Determination of Alkali Metals as the Sulfate

The decision to develop the bromine trifluoride scheme opened the way to a simple and reliable method for determining the alkali metal content of tungsten bronzes. It was noted in an earlier section that the alkali metal will be converted into its tetrafluorobromate(III) when a bronze sample is

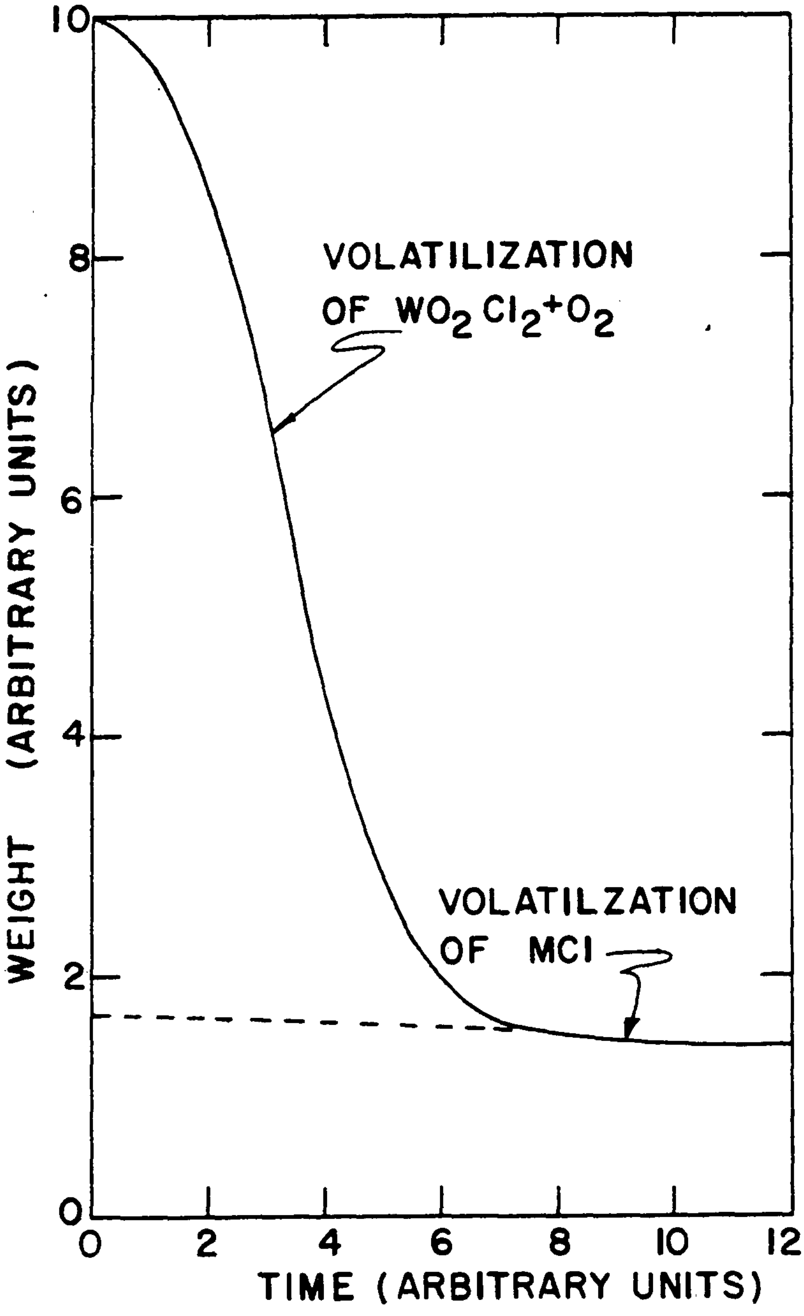

Figure 3. Weight losses of tungsten bronzes during chlorination

treated with bromine trifluoride. Alkali metal tetrafluorobromates(III) are easily converted, in turn, to alkali metal sulfates which are good weighing forms for the alkali metals.

1. Recovery of alkali metals from fluorides

Proof of the reliability of this method was made in two series of experiments. The first series demonstrated that alkali metal fluorides can be removed from the reactor vessel and the alkali metal gravimetrically determined as its sulfate. A known quantity of a standardized alkali metal fluoride solution was pipeted into a reactor tube; care was taken to distribute the solution over most of the interior surface to duplicate actual recovery conditions. Then the fluoride solution was evaporated *in situ* so that solid alkali metal fluoride coated the wall of the reactor. A 0.5 *N* solution of sulfuric acid was used to rinse the fluoride into a weighed platinum dish. Flame tests were used to indicate when the rinsing operation was complete. The rinsings were fumed to dryness on a hot plate, then ignited with the full flame of a Meeker burner for about two minutes. The dish was cooled in a desiccator and weighed. The amount of alkali metal was calculated from the recovered sulfate. Table 5 gives the results of these experiments.

2. Determination of alkali metals in tungstates

The second series of experiments demonstrated the ability

Table 5. Alkali metal fluoride recoveries

Alkali metal fluoride	Mg metal added	Mg metal recovered	Difference (mg)
LiF	0.38	0.40	+0.02
		0.37	-0.01
	3.83	3.83	0
		3.82	-0.01
	7.65	7.64	-0.01
		7.65	0
NaF	0.23	0.23	0
		0.23	0
	2.30	2.33	+0.03
		2.32	+0.02
	23.00	23.00	0
		23.04	+0.04
KF	0.39	0.39	0
		0.39	0
	3.91	3.90	-0.01
		3.84	-0.07
	39.12	39.10	-0.02
		39.12	0
		39.17	+0.05
		39.07	-0.05
RbF	0.78	0.77	-0.01
		0.77	-0.01
	7.81	7.81	0
		7.88	+0.07
	78.11	78.17	+0.06
		78.05	-0.06
CsF	0.81	0.81	0
		0.81	0
	8.14	8.15	+0.01
		8.08	-0.06
	81.39	81.31	-0.08
		81.46	+0.07

to decompose alkali metal tungstates and to quantitatively measure their alkali metal content. The tungstate (0.2-0.5 gram) was weighed into a small Teflon cup. The cup was put into a reactor tube and the tube was attached to the fluorination apparatus. After bromine trifluoride was transferred into the reactor and the reaction was complete, the oxygen was pumped into the oxygen measuring subsystem and the other volatiles were returned to the reagent still. When the reactor tube had been removed from the apparatus, the residue in the tube was rinsed into a platinum dish with 0.5 N sulfuric acid.

At this point, there was a change in the procedure. Bromine trifluoride dissolved a small amount of the nickel, etc., from the flange and the still column. This extraneous metal was removed by a simple ion exchange separation on Dowex 50-X4 cation exchange resin. The rinsings were fumed to drive off bromine and hydrofluoric acid, then diluted with water. This sulfuric acid solution was percolated through a Dowex 50 column. The eluant was 0.5 N sulfuric acid. Flame tests of the effluent showed when the alkali metal was eluted; the nickel, copper, etc., remained on the column. The effluent was fumed to dryness and ignited in a weighed platinum dish. After cooling and weighing the dish and its contained sulfate, one could calculate the amount of alkali metal in the sample. Table 6 contains examples of the results obtained with alkali metal tungstates.

Table 6. Determination of alkali metal in tungstates

Alkali metal tungstate	Mg metal added	Mg metal recovered
Li[a]	24.9	24.9
	43.5	43.2
Na	63.3	63.2
	84.0	84.3
K	75.7	75.8
	93.4	93.5

[a] The composition of this material was established by the scheme outlined in Figure 9.

IV. DETERMINATION OF THE OXYGEN

The method, which is described in this chapter, is the only method which was tried for the determination of oxygen in the alkali metal tungsten bronzes. The work is divisible into two parts. The first part is the procedure for calibration of the oxygen measurement subsystem and the second part is proof of the method by actual determination of oxygen in tungsten trioxide and alkali metal tungstates.

A. Calibration of the Oxygen Measurement Subsystem

It will be helpful to refer to Figure 2 during the reading of this section and the next. Locate the calibration bulb and note that it is attached just ahead of the Töpler pump via two stopcocks and a standard-taper joint. There are two of these bulbs. One is about 50 milliliters and the other is about 150 milliliters in volume; these allow some flexibility in weighing oxygen samples. A calibration bulb is the means of providing known weights of oxygen for the calibration procedure.

The device of Figure 4 was used to load the calibration bulbs with known quantities of oxygen. An evacuated and weighed bulb was attached to the bulb loader via the standard-taper joint. After evacuating the whole device, the pump was isolated and the oxygen cylinder was opened until the gauge indicated some pressure between 0 and 1520 mm (-30 inches to

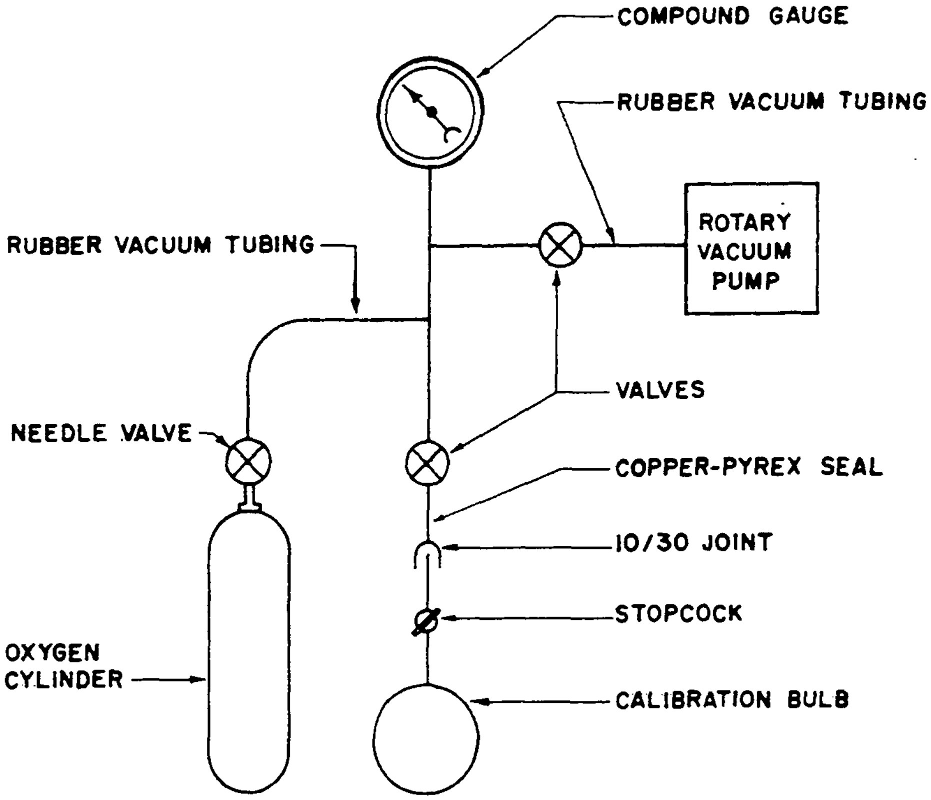

Figure 4. Device for loading the calibration bulbs

+15 pounds/inch^2). The bulb was isolated, removed and weighed. The weight difference of the bulb was the weight of oxygen. The joint was rendered greaseless for each weighing. A record of the gauge pressure and the corresponding weight of oxygen was useful because these data could be utilized for quickly and systematically obtaining certain, desirable quantities of oxygen in the bulbs.

The loaded bulb was attached to the fluorination apparatus via the previously indicated joint. After the Töpler pump, containment bulbs, and manometers were fully evacuated, the desired combination of containment bulbs was selected and the Töpler pump was used to transfer the oxygen from the calibration bulb into the chosen combination of containment bulbs. The pump was operated for a few strokes after no more gas was observed to bubble through the exhaust float valve. The pump was shut off on the exhaust stroke and the mercury was allowed to rise through the stopcock above the float valve and into the section of capillary tubing above the stopcock. The stopcock, when closed, held the mercury at a fiducial mark on the capillary.

After isolating the measuring manometer from the manifold, air was bled through the transfer bleed until the transfer manometer was balanced on the two fiducial marks which indicate equal pressure in both arms of the manometer. These marks were established by known equal pressures (both arms *in vacuo* or at atmospheric pressure) or by a bubble level. The transfer manometer is long enough to contain a one atmosphere pressure difference in either direction. Finally, one observed the pressure reading on the measuring manometer. Note that corrections must be applied for the density variation of the oil in the measuring manometer with temperature and for the P-T relation of the oxygen in the containment bulbs. In this work, pressures were corrected to 25°C for the calibration curves. Figure 5 shows a typical family of calibration curves.

B. Determination of Oxygen in Tungsten Trioxide and Tungstates

A sample of oxide, tungstate, or bronze, which contained less than 330 milligrams of oxygen, was weighed into a Teflon sample cup and the cup was placed in a reactor tube. The reactor was assembled and evacuated to remove air and water vapor. About ten milliliters of bromine trifluoride were transferred into the reactor. For this operation, the reactor was refrigerated with liquid nitrogen and the reagent still pot and column were heated. When sufficient bromine trifluoride was in the reactor, the reactor was isolated and allowed to attain room temperature. Usually, the reactor was filled in the evening and the products removed the next morning.

When an oxygen measurement was made, the following

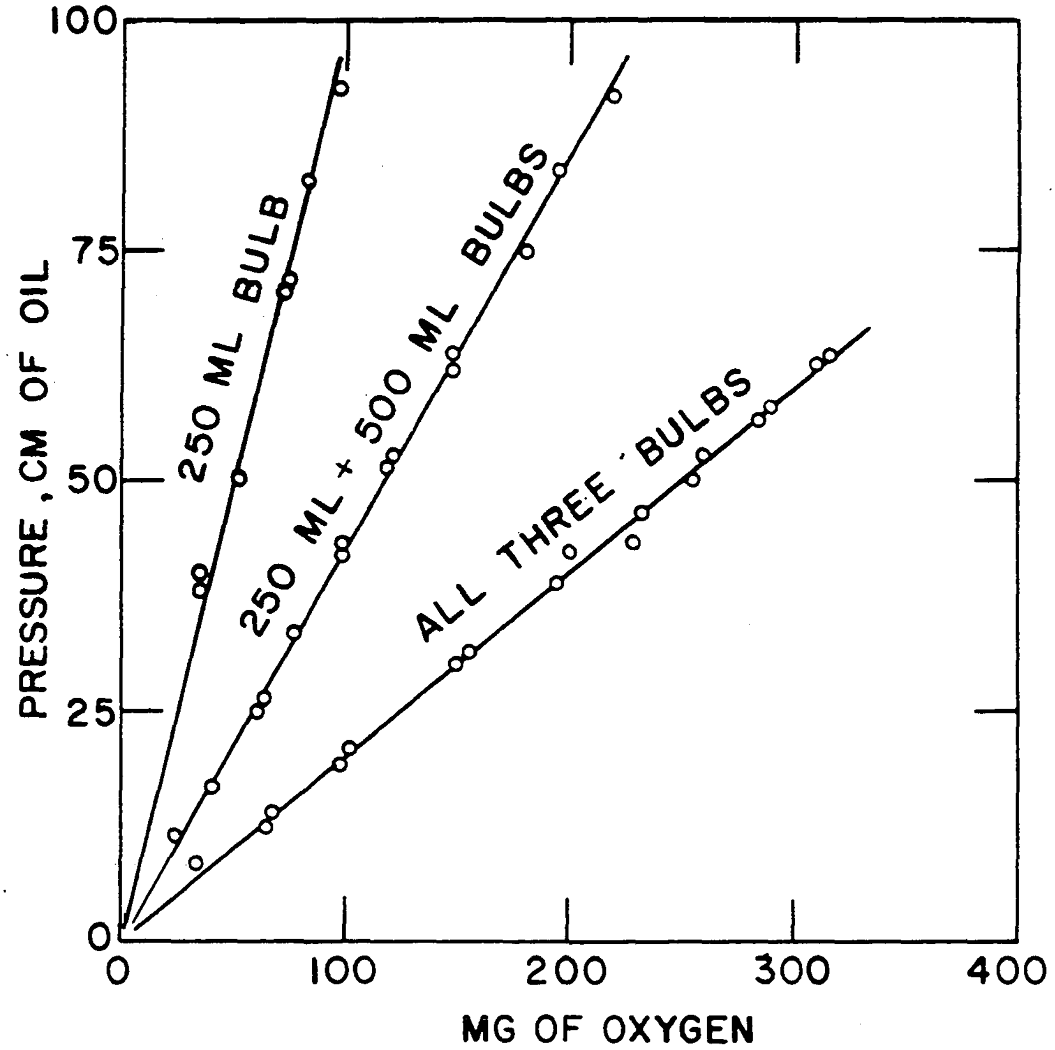

Figure 5. Sample calibration curves for the oxygen-measuring subsystem

procedure was employed. First, the reactor was packed in a dry ice and acetone bath. This froze the bromine, excess bromine trifluoride, and tungsten hexafluoride so that there would be less burden on the two traps between the reactor and the Töpler pump. These two traps were also packed with the same refrigerant to protect mercury and glass from fluorine compounds. While the traps cooled and the reactor contents froze, the pertinent lines, Töpler pump, appropriate containment bulbs, and manometers were evacuated. In about 15-20 minutes, the manometers and containment bulbs were isolated from the manifold and the Töpler pump was used to transfer the oxygen from the reactor to the containment bulbs for measurement. Beyond this point, the measurement was carried out in the same manner as it was in the calibration procedure. A summary of these results appears in Table 7.

Table 7. Determination of oxygen in tungsten trioxide and tungstates

Compound	Mg oxygen added	Mg oxygen[a] found
WO_3	57.6	57.8 ± 0.5
	70.6	70.5 ± 0.6
	86.4	85.8 ± 0.7
	116.5	117.4 ± 1.0
	163.0	163.5 ± 1.3
Li_2WO_4[b]	133.7	134.1 ± 1.1
	233.6	232.5 ± 1.9
Na_2WO_4	88.0	88.4 ± 0.7
	116.9	117.3 ± 1.0
K_2WO_4	61.7	62.0 ± 0.5
	62.0	61.7 ± 0.5

[a] The ± value is derived from the statistics of the calibration.

[b] The composition of this material was established by the scheme outlined in Figure 9.

V. DETERMINATION OF THE TUNGSTEN

Although tungsten has been known since 1783 and much use is made of it and its compounds, relatively little is actually known about the fundamental chemistry of the element. In many respects, the analytical chemistry of tungsten seems to be rather poorly studied. A search through the analytical literature revealed that about 400 papers have been published concerning the determination of tungsten. However, only four of these publications attempt to intercompare methods and only one considers the problem of suitable standards upon which to base analytical methods.

A. Analytical Standards for the Determination of Tungsten

1. Tungsten metal

Until recently, it was most difficult to obtain tungsten of sufficient purity to serve as an analytical standard. Combinations of zone refining, hexahalide distillation, and hexahalide decomposition now make excellent quality tungsten metal available (68, 85, 89, 114). Unfortunately, the dissolution of tungsten is awkward and the resulting solutions are often inconvenient, especially if they contain fluoride ion. It is better, therefore, to seek more useful standard compounds unless one wishes to use the metal as a starting material for the preparation of standard compounds.

2. Sodium and potassium tungstates

Duval (39) reports that sodium tungstate can be used as a standard compound, if it is dried at a temperature greater than 150°C. This work confirms that it is, indeed, a good standard because it can be obtained in a thoroughly anhydrous condition and its composition is truly Na_2WO_4. This work has also employed potassium tungstate as a standard and found it to be satisfactory in every respect.

3. Tungsten trioxide

This compound is extremely interesting, not only because it is a useful standard compound, but also because it is a good weighing form for the gravimetric determination of tungsten. Furthermore, interest has been intensified by controversies about its stoichiometry and volatility.

Tungsten oxidizes rather easily when heated in air or oxygen to form tungsten trioxide, WO_3. This oxide can also be prepared from aqueous tungstate solutions, although there is some doubt about the composition of the product (54); it is probably best considered to be the hydrated oxide or hydrated tungstic acid. Conversely, tungsten trioxide dissolves in strongly basic solutions to form tungstate, provided that the oxide has not been too strongly ignited.

There are two problems in the preparation of tungsten trioxide which have challenged its use as the conclusion for gravimetric procedures and have reduced its value as a standard compound of tungsten. The first problem is that of stoichiometry. It is possible to prepare the whole range of oxides whose oxygen-to-tungsten ratio varies from nearly zero to 3.000 (2, 25). It has been reported in the literature (50, 87, 140) and confirmed in this laboratory that tungsten trioxide loses oxygen, due to the reduction of tungsten, when it is exposed to heat, light, or other reductants.

Explanations for the composition range and structures of tungsten oxides are found in the literature (2). Each tungsten atom is octahedrally surrounded by six oxygen atoms. In the trioxide, these WO_6 units are joined by corners only; but as the oxygen-to-tungsten ratio decreases, the WO_6 units become more intricately joined in combinations of corners, edges, and faces to form chains and slabs. The loss of each oxygen atom from the oxide lattice means that two electrons are added to the conduction band of the lattice and it is meaningless to speak of definite tungsten(IV) and tungsten(V) atoms in such a lattice.

The second problem is found in the volatility of tungsten trioxide. It has been reported that this oxide is volatile above 750-800°C (14; 82; 83; 120, p. 1038); it is also reported that it is not volatile below 1400-1500°C (9; 105, pp. 172-186). Perhaps it is significant that there is a transition between the alpha and beta forms of the oxide at 800°C (57). The presence of water vapor increases the volatility (9).

Two series of experiments were performed to establish the behavior of tungsten trioxide as a function of temperature. The first series was a thermogravimetric study of tungsten trioxide. In this study, the oxide became anhydrous about 100°C and began to lose weight at 650°C. At 1200°C, there was a great and sudden increase in the rate of weight loss. Figure 6 is a thermogram of tungsten trioxide.

The second series of experiments was designed to study the relations between volatility and stoichiometry. Because this work was performed in platinum boats, it was necessary to demonstrate that platinum boats retained constant weight during all the operations of the experiments. Once the boats had been ignited in air at 1200°C, they kept constant weight thereafter throughout both oxidation and reduction procedures. It was necessary, too, to dry the tungsten trioxide at 500°C for an hour in an oxygen atmosphere in order to guarantee perfect dryness. Before drying, the oxygen-to-tungsten ratio was 3.023 ± 0.003 and after drying the ratio was 2.997 ± 0.005.

A sample of tungsten trioxide was weighed into a weighed platinum boat. After the oxide was exposed to air for a known period of time and at a known temperature (measured by optical pyrometer and thermocouple), the boat was cooled and weighed to determine its total weight loss. Next, the oxide was reduced by hydrogen at 800°C. The third and final

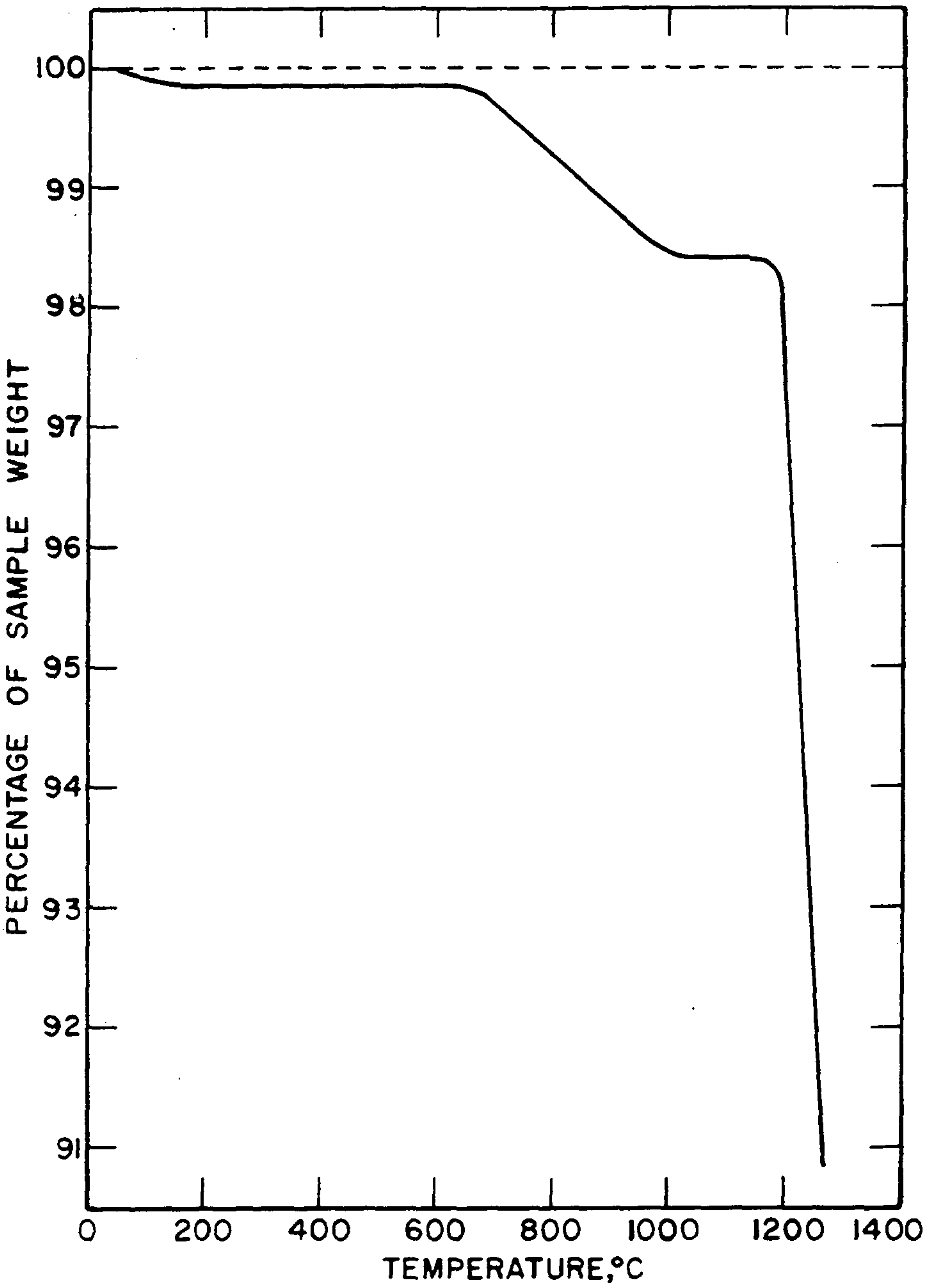

Figure 6. Thermogravimetric behavior of tungsten trioxide

weighing measured the amount of tungsten which remained after the ignition. Calculations based on these three weights determined how much of the oxide was volatilized and how much weight loss occurred via changes in stoichiometry. Figure 7 is a graphic presentation of these results.

One more result of this work is the development of a procedure for the preparation of tungsten trioxide. One stirs an excess of commercial tungsten trioxide or tungstic acid into a concentrated solution of ammonia. Stirring is continued for 12-24 hours in the presence of filter pulp. The slurry is filtered and the filtrate is saved for the next step. Add 30% hydrogen peroxide to the filtrate until it reaches its maximum yellow color (one of the peroxytungstates) and then add concentrated nitric acid until the solution is about 5 M in nitric acid. Allow the solution to stand on a hot plate operating at a low heat until precipitation of the yellow tungstic acid hydrate is complete. Filter out the solid and use it to begin a new cycle of solution and precipitation. This cycle is repeated two or three times. The last precipitate is ignited in oxygen at 500-600°C and stored in a black bottle in a desiccator. The material so prepared has an oxygen-to-tungsten ratio of 3.000 ± 0.005.

B. Titrimetric Determinations of Tungsten

This is a brief description of several unsuccessful attempts to determine tungsten by titration. In each case,

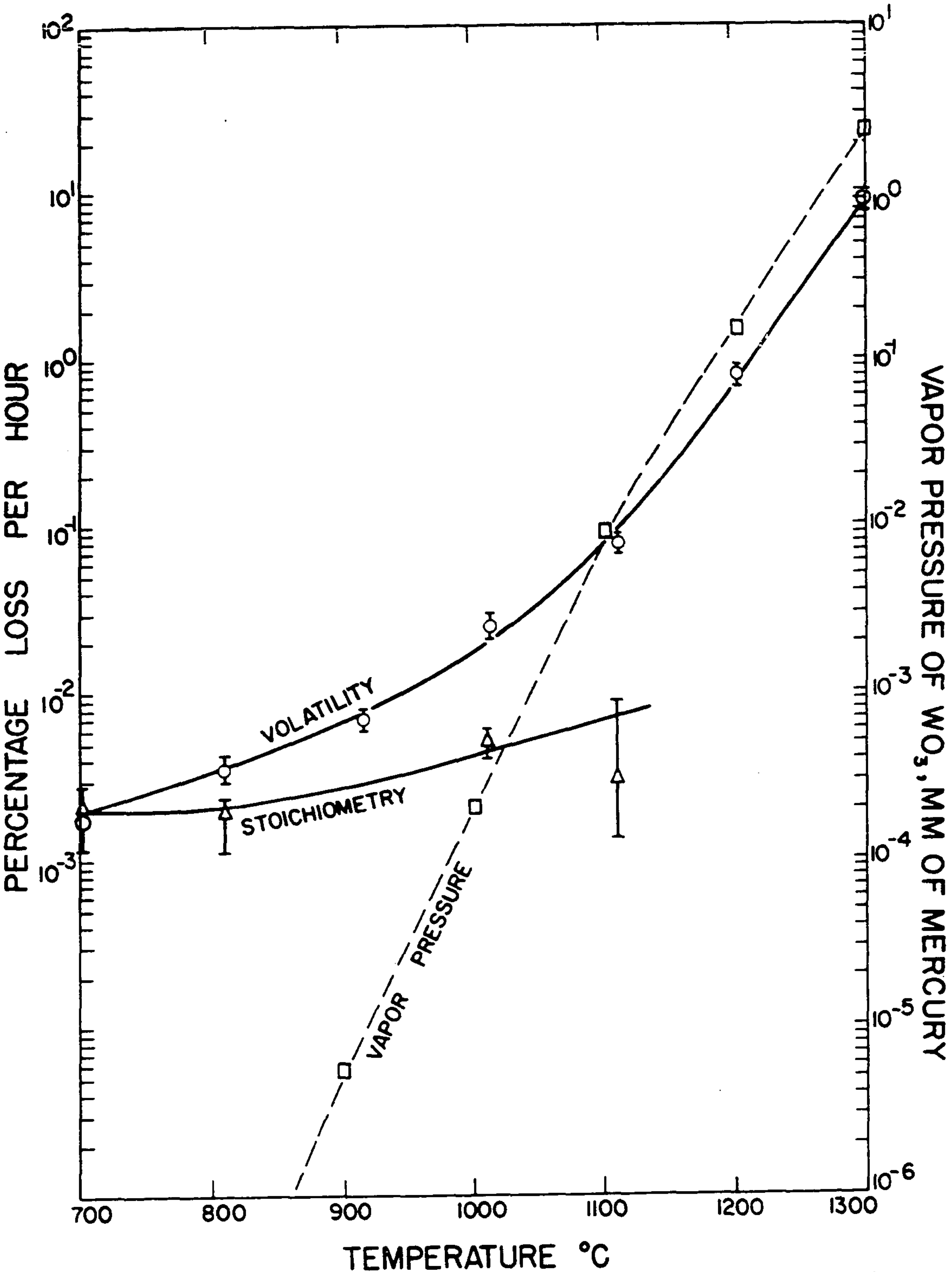

Figure 7. Weight losses of tungsten trioxide as functions of temperature

the difficulties which defeated the method are discussed. Table 9 summarizes all the titrations which were tried.

1. Precipitation titrations

All these titrations employed the heavy metals silver, mercury, and lead as titrants for precipitation reactions with tungstate (60, 103, 107). In all cases, the results were so badly complicated by the effects of pH, buffer system, tungstate concentration, and the end point detection methods that it was impossible to make practical use of the titrations.

2. Acid-base titrations

Attempts to titrate tungstate ion with hydrogen ion to form bitungstate failed because of the pH dependence of the polytungstate system (11, 13, 22, 135). The several species of polytungstates form at widely different rates and the end point of this type of titration cannot be readily located. Near the end point, the pH drifts rapidly and erratically in both directions while tungstate ion polymerizes. Further, the drifting occurs over too long a time interval (hours) to allow one to wait for the attainment of equilibrium.

3. Redox titrations

It was demonstrated that vanadyl(IV) and ascorbic acid are not useful reducing titrants. These titrations, like the precipitation titrations, are confused by pH, buffer systems, etc. Actually, however, some of the potentiometric redox titrations reported in the literature appear to have a real potential for the determination of tungsten. Especially recommended for future development are direct titrations like the one in which tungsten(VI) is reduced to tungsten(V) by chromium(II) in 10 M hydrochloric acid solution (26, 42, 52).[2]

4. Conductometric titrations in bromine trifluoride solution

Conductivity of compounds in bromine trifluoride solution and the performance of conductometric titrations in this solvent system are not new ideas (47, 138). It was pointed out in Section II.A.2 that this solvent has an acid base chemistry. Table 8 gives some analogies between the water and bromine trifluoride systems.

These titrations were performed in Teflon beakers. The buret was either Kel-F or Pyrex (equipped with a Teflon stopcock); the Pyrex buret was badly etched and bubbles of oxygen and silicon tetrafluoride were observed rising through the titrant solution. The smooth, shiny platinum electrodes appeared to be unaffected by immersion in bromine trifluoride. The titration equipment, except for the conductivity bridge, was contained in a glove box and maintained in an atmosphere of dry nitrogen. A Leeds and Northrup conductivity bridge measured the conductivities. Titrations of several acids and bases were not particularly successful: SbF_5-KF, SbF_3-BaF_2,

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[2] Brown, T. Ames Laboratory, Ames, Iowa. Titration of tungstate with chromous chloride. Private communication. 1962.

Table 8. Acid-base analogies between water and bromine trifluoride

Item	Water system	Bromine trifluoride system
Acid	H^+, H_3PO_4	BrF_2^+, BrF_2PF_6
Base	OH^-, KOH	BrF_4^-, $KBrF_4$
Salt	K_3PO_4	KPF_6
Basic oxide	K_2O	KF
Acidic oxide	WO_3	WF_6
Oxyanion	$WO_4^{=}$	$WF_8^{=}$
Solvent ionization	$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$	$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$
Neutralization	$2\ KOH + H_2WO_4 \longrightarrow$ $K_2WO_4 + 2\ H_2O$	$2\ KBrF_4 + (BrF_2)_2WF_8 \longrightarrow$ $K_2WF_8 + 4\ BrF_4$

SbF_5-AgF, and WF_6-AgF. Tungsten hexafluoride partially volatilized out of the bromine trifluoride solutions, so that these titrations were of no use. Curiously, both barium fluoride and silver fluoride formed precipitates with tungsten hexafluoride.

C. Spectrophotometric Determinations of Tungsten

It had been observed earlier, during the attempt to use ascorbic acid as a titrant, that tungstate reacts with ascorbic acid to produce a brown solution. This led to the

Table 9. Summary of titrimetric attempts to determine tungsten

Titrant	Indicator electrode	Reference electrode	Description of the titration
$AgNO_3$	Ag	S.C.E.	Potentiometric precipitation of Ag_2WO_4
$Hg(NO_3)_2$	Pt	S.C.E.	Potentiometric precipitation of $HgWO_4$
$Pb(NO_3)_2$	Ag	Ag	Amperometric precipitation of $PbWO_4$
$Pb(NO_3)_2$	W	S.C.E.	Potentiometric precipitation of $PbWO_4$
$Pb(NO_3)_2$	Pb	S.C.E.	Potentiometric precipitation of $PbWO_4$
$Pb(NO_3)_2$	Pt	S.C.E.	Potentiometric precipitation of $PbWO_4$
$Pb(NO_3)_2$	Pt	S.C.E.	Potentiometric precipitation of $PbWO_4$ using a $Fe(CN)_6^{-3}$-$Fe(CN)_6^{-4}$ indicator system
HCl	Glass	S.C.E.	Potentiometric pH
$HClO_4$	Glass	S.C.E.	Potentiometric pH
$VOCl_2$	Pt	S.C.E.	Potentiometric redox
Ascorbic acid	Pt	S.C.E.	Potentiometric redox
AgF	Pt	Pt	Conductometric

idea of a possible spectrophotometric method and an investigation was begun to examine the properties of this brown color. As one might have expected for aqueous tungstate solutions, it was found that the visible and ultra-violet absorption spectra of the tungstate-ascorbic acid complex were much complicated by pH, buffer system, etc. In addition, the molar extinction coefficient was very low, less than 50, and this particular system could not be used for the determination of tungsten.

One attempt was made to utilize the colored ions produced when tungsten(VI) is reduced by tin metal in strong hydrochloric acid solutions. In such a case, the solution changes from colorless, through blue and red, to olive green. None of the intermediate colors was stable enough. The greenish nonachloroditungstate(III) ion, $W_2Cl_9^{\equiv}$, fades rapidly with time, even in the reducing solution. Fluoride ion interferes seriously with the reduction by causing tungsten(V) to become much more stable; even so, there is insufficient color stability at this stage for a spectrophotometric method.

D. Coulometric Determination of Tungsten

A promising area of research appears to be the application of coulometry to the determination of tungsten. Experiments showed that it is probably not possible to use a constant current coulometer. However, it may be quite feasible to use a controlled potential instrument for analysis and it is recommended that the possibility be investigated.

There are no known reports in the literature which discuss or describe a coulometric method for tungsten.

It is known that the lower oxidation states of tungsten are most stable in the presence of chloride ion for the formation of complexes and with hydrogen ion to assist in lowering the reduction potential (55). Inefficient reductions were accomplished in various lithium chloride-hydrochloric acid media. The particular medium determined which oxidation state of tungsten was attained.

The reduction potential of tungsten(VI) compounds occurs in the range from +0.3 to +0.05 volt (70; 73, p. 124; 74). This conflicts with the reduction of hydrogen, because of the requirement for a high concentration of hydrogen ion in tungsten reductions. In these strongly acid solutions, the reduction potential of hydrogen is more positive than 0 volt. Furthermore, it is difficult to find an inert electrode with a high enough hydrogen overpotential and which will not react with hydrogen ion or reduce tungsten in strong acid (41). In many cases, it is possible to prevent the reduction of hydrogen by using a suitable chemical potential buffer. Several combinations of buffers and catholytes were tried in efforts to discover a practical system. But there are no reduction potentials between those of hydrogen and tungsten in suitable catholytes. The couples $TiOCl_2$-$TiCl_3$ (72, 80), H_2SnCl_6-H_2SnCl_4, and $Co(NH_3)_6Cl_3$-$CoCl_2$ have potentials close to that for $WO_2Cl_4^-$-$WOCl_4^-$, but they are not negative enough. Hence, a controlled potential coulometer should be valuable for solving this problem.

E. Gravimetric Determinations of Tungsten

Gravimetric analytical methods for the determination of tungsten are divided into three principal categories: precipitation of tungstate by metal ions, precipitation of tungstate by organic reagents, and precipitation of tungstic acid by the acidic hydrolysis of tungstate.

Aluminum, barium, beryllium, calcium, chromium, cobalt, copper, iron, mercury, magnesium, nickel, lead, strontium, thorium, and zirconium form insoluble salts with tungstate and have been used as cationic precipitants for the determination of tungsten (23, 40). This laboratory and at least one other have found that calcium, barium, lead, and nickel are not effective precipitants. The precipitation of insoluble tungstates is a typically complicated situation which is influenced by pH and the presence of other anions and complexing agents (10, 53, 71, 84). pH interferes through the formation of basic salts and the formation of polytungstates. The precipitations are sensitive to buffer types and concentrations, as well as the concentrations of tungstate and the metal ion. Finally, either the precipitations are incomplete or else the precipitate compositions are too indefinite for use as weighing forms.

Organic reagents have faults. Some of them are expensive or are toxic drugs like codeine and strychnine. All of them probably cause incomplete precipitation. And many of the precipitates have indefinite compositions which force one to ignite them to tungsten trioxide, a procedure which too few workers perform correctly. Common organic reagents are 8-quinolinol, α-benzoinoxime, and cinchonine (23, 40). Cinchonine and α-benzoinoxime have been found unsatisfactory because they definitely do not quantitatively precipitate tungsten (28, 66, 95). The literature reports dozens of other precipitants: amines, alkaloids, dyes, gelatin, etc.

Strong mineral acids have been employed to precipitate tungstate as tungstic acid hydrate. It is claimed that good results are obtained with hydrochloric acid, perchloric acid, nitric acid, sulfuric acid, and nitric acid-hydrogen peroxide mixtures (23, 36). To the contrary, all these reagents have been considered deficient (28). Incomplete precipitation does occur in hydrochloric acid because of the formation of anionic tungstate complexes and tungstenyl derivatives (43, 44). In any case, the composition of the tungstic acid precipitate is indefinite and it must be ignited to the trioxide.

1. Precipitation in a nitric acid-hydrogen peroxide solution

The work of Dams and Hoste (36) has been adapted as a basis for a very successful wet chemical method for determining tungsten. Dahmer[3] has worked out the conditions under which the precipitation of tungsten is quantitative. The work reported in this thesis provided the standards which were used to check the method and discovered the conditions for igniting the precipitate to tungsten trioxide.

The compounds involved in this research contained no interferences for the method; therefore, the application was very simple. If the compound to be analyzed was a bronze or oxide, the compound was decomposed in a basic, oxidizing fusion. The fusion mixture was about 75 weight per cent sodium hydroxide and 25 weight per cent sodium nitrate. After the fusion the melt was dissolved in water. If the compound was a tungstate, it was dissolved in water directly. Each analysis started with 0.2 to 0.5 gram of compound and about 100 milliliters of water. Thirty per cent hydrogen peroxide was added to the solution until the maximum yellow color was developed. Fifty milliliters of concentrated nitric acid were added and the solution was heated on a hot plate (60-90°C) until precipitation from the homogeneous solution began. The heating continued for two more hours to digest the precipitate. The solution was cooled and filtered through a weighed Selas crucible; the rinsing solution was 2 M nitric acid. The crucible was dried at 100°C for half an hour, then was ignited in a muffle furnace (air atmosphere)

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[3] Dahmer, L. H. Ames Laboratory, Ames, Iowa. Precipitation of tungstate as tungstic acid. Private communication. 1963.

for an hour at 500°C. When the crucible had cooled for an hour in a desiccator, it was weighed again and tungsten was calculated from the tungsten trioxide in the crucible. Table 10 compares the results obtained for potassium tungstate by the nitric acid-hydrogen peroxide and hydrogen reduction methods.

Table 10. Determination of tungsten in potassium tungstate

Operator	Method	No. of detns.	Sample size (gm)	Per cent tungsten found
	Theory			56.39
Dahmer	HNO_3-H_2O_2	4	0.10-0.13	56.33 ± 0.03
Raby	H_2 Redn.	5	0.12-0.22	56.34 ± 0.05

2. Hydrogen reduction

This has been a very valuable analytical method for the determination of tungsten in certain of its compounds, especially in oxides, tungstates, and bronzes (90, 91, 123, 124, 126, 141). The method was simple; 0.2 to 0.5 gram of the compound was weighed into a weighed reaction boat. The boat was inserted into a tube furnace and the furnace was flushed with helium for 10-15 minutes. Then, hydrogen was put through the tube at a rate of about 250 cubic centimeters per minute and the heat was turned on. The operating temperature was 650-825°C. When the reaction was judged to be complete, the heat was turned off and the furnace was allowed to cool for an hour or an hour and a half. As soon as the furnace was cool, it was flushed again with helium for about 15 minutes. The boat was removed and weighed. This procedure was repeated until the boat and its contents reached constant weight. The boat contained pure tungsten metal. The reaction is indicated by the equation:

$$M_xWO_3 + (3 - \frac{x}{2})H_2 \longrightarrow \frac{x}{2} M_2O + W + (3 - \frac{x}{2})H_2O. \qquad (5)$$

It was obvious from the start that construction materials would have to be chosen for their ability to withstand hot hydrogen. Of the ceramic materials tested, only Vycor and quartz were chosen. They were employed for furnace tubes, but the tubes needed replacement every three or four weeks to prevent the development of destructive cracks. All the other ceramics (silica, alundum, zirconia, and porcelain) were too porous for furnace tubes or they flaked and cracked. Metals have been the mainstays of construction materials. Gold was considered; it displayed a small hydrogen absorption, but its melting point is too low. Platinum was useful, but it is expensive. Type 303 stainless steel showed weight gains and a diffusion of its constituents which caused the surface to "bloom". Nickel, molybdenum, and tungsten had small

Table 11. Absorption of hydrogen by metals

Metal	Hydrogen absorption (ppm)
Au	1.5
Mo	12.1
Ni	1.5-3.0
W	0.8-0.9

capacities for absorbing hydrogen. Table 11 shows the absorption of hydrogen by these metals.[4] It is important to note that tungsten absorbs a negligible amount of hydrogen (1; 35; 120, p. 1031).

The equipment, which was used for these hydrogen reductions, is schematically diagrammed in Figure 8. The molybdenum liner in the Vycor tube prevented flakes of silicon from falling into the sample boats. Silicon formed in the reaction of hydrogen with the Vycor. In addition, thermal stresses caused chips of Vycor to flake away from the interior of the tube. The liner had to be replaced at the same time as the tube because heating rendered the molybdenum too brittle to be removed without breaking. The

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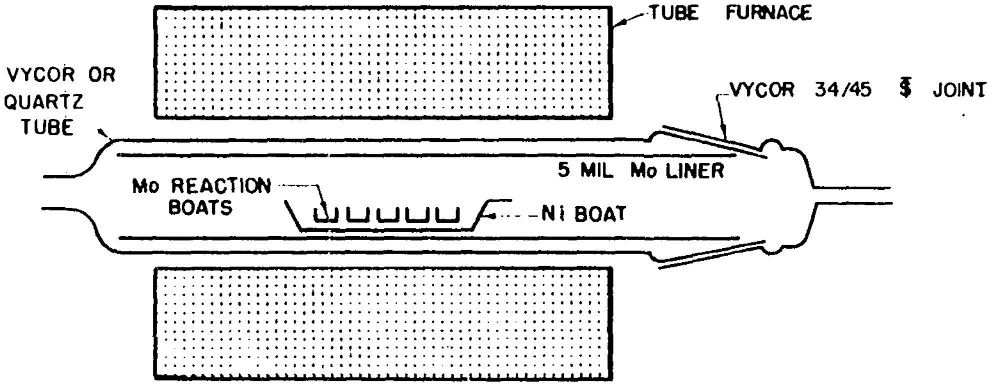
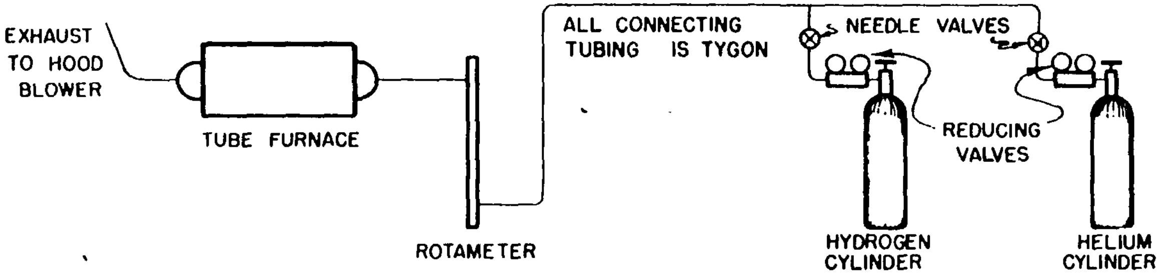
[4] Kamin, G. J. Ames Laboratory, Ames, Iowa. Determination of hydrogen in metals. Private communication. 1960.



A. DETAIL OF FURNACE



B. ENTIRE REDUCTION SYSTEM

Figure 8. Schematic diagram of the hydrogen reduction apparatus

sample boats were folded out of three mil molybdenum sheet: eight by eight millimeters and five millimeters deep. They were light in weight (about 0.3 gram), durable, and inexpensive. Up to six of these molybdenum sample boats could be placed in a conventional nickel boat. This was convenient for handling the sample boats during insertion into and removal from the furnace.

Many tungsten compounds were analyzed by the hydrogen reduction method. Table 12 presents the details of these analyses. It had already been demonstrated that there was no complication by absorption of hydrogen in tungsten metal. However, it was necessary to demonstrate that no alkali metal remained in the metallic tungsten after reduction. Spectrographic analysis of the reduced tungsten[5] and investigation of alkali metal behavior showed that no weighable amount of alkali metal remained. These data are included in Table 12. Lithium is the exception and will be discussed below. The method is slow, but the alkali metal and oxygen can be determined by the bromine trifluoride method during the same time that tungsten is being determined by hydrogen reduction and several replicates can be reduced simultaneously.

The low volatility of lithium oxide has essentially defeated hydrogen reduction methods for determining tungsten

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[5] DeKalb, E. L. Ames Laboratory, Ames, Iowa. Determination of alkali metals in tungsten. Private communication. 1963.

Table 12. Determination of tungsten by hydrogen reduction at 825°C

Compound[a]	% tungsten theory	% tungsten found	Hours to completion
WO_3 (Raby)	79.30	79.32 ± 0.03	1
WO_3 (Fisher, 783243)	79.30	79.27 ± 0.20	1
WO_3 (VarLacOid, A-2-4039)	79.30	79.28 ± 0.08	1
WO_3 (Amend, C607512)	79.30	79.22 ± 0.10	1
WO_3 (North Metal & Chem. Co., 116)	79.30	79.12 ± 0.35	1
Li_2WO_4 (Gallard-Schlessinger)	70.24	87.59 ± 0.03	(13)
Na_2WO_4 (J.T. Baker, 4461)	62.57	62.50 ± 0.25	27
K_2WO_4 (A.D. McKay)	56.39	56.34 ± 0.05	120
$Rb_6W_6O_{21}$ (Raby)	56.51	55.93 ± 0.46	35
Cs_2WO_4 (Gallard-Schlessinger)	35.79	35.75 ± 0.14	40
Li_2O (A.D. McKay, and Raby)	loses 0.083%/hr.		(55)
Rb oxides (Gallard-Schlessinger)	completely volatile		12
Cs oxides (Gallard-Schlessinger)	completely volatile		6

[a] The parentheses enclose the name of the manufacturer and the lot number, if that is known.

in lithium compounds. Therefore, it has been found expedient to determine tungsten in lithium tungstates and bronzes by the nitric acid-hydrogen peroxide method given in Section V.E.1. It is apparent from the entries for lithium tungstate and lithium oxide in Table 12 and the diagram of Figure 9 that only one half of the tungsten is reduced and one half of the lithium appears as free oxide; the other half of both lithium and tungsten seems to remain unaffected by the reduction. No explanation is offered for this phenomenon. This work confirms the observations of other workers (125, 133) that the lithium bronzes and tungstates are much more resistant to chemical attack than the other alkali metal compounds.

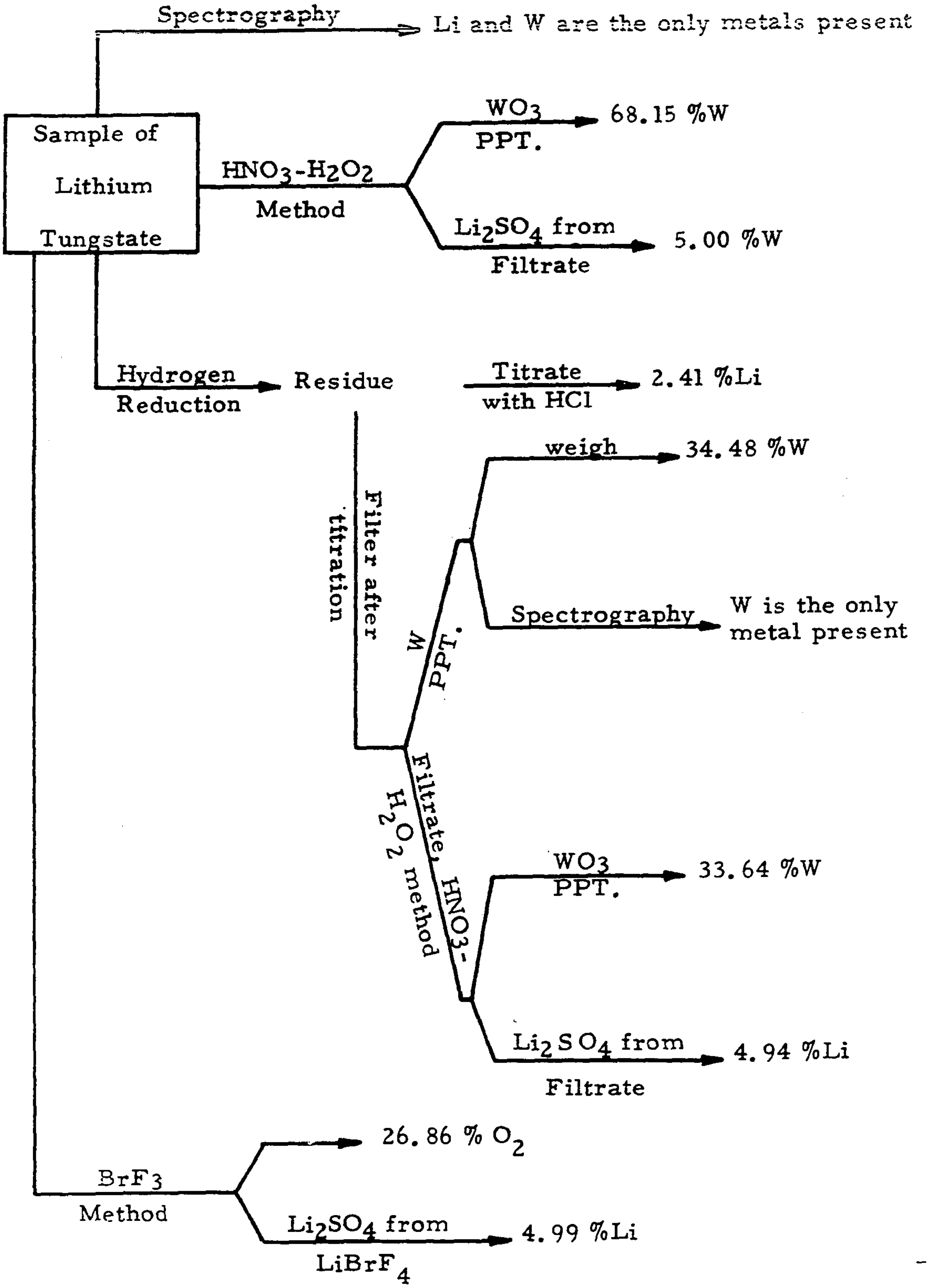

Figure 9. Analytical scheme for lithium tungstate

VI. SUMMARY AND CONCLUSIONS

A. Summary of Data for Tungsten Trioxide and Tungstates

The data derived from analyses of tungsten trioxide and alkali metal tungstates have been gathered into one collection. These data are presented in Tables 13 and 14. There are a few things to notice. First, the tungsten trioxide samples show some variation in composition. It is thought that this phenomenon is probably due to the water contained in the different preparations, although no specific effort was made to prove the idea. Second, the composition of lithium tungstate is appreciably different than that expected for the orthotungstate, Li_2WO_4. The proof was given in the last section of Chapter V; the interpretation of this particular composition is not known. Third, the value of 4.018 for the oxygen-to-tungsten ratio of sodium tungstate could be an artifact; there is no other reason to believe that the ratio is actually not 4.000. Finally, the preparation of rubidium tungstate, which was made in this laboratory, has a composition nearer to $Rb_6W_6O_{21}$ than to Rb_2WO_4. This salt corresponds to the known $Na_6W_6O_{21}$, but it has not been reported in the literature.

B. Summary of Data for Bronzes

The data obtained from analyses of bronzes have been collected into a separate summary. Aside from the fact that the composition data are useful to the solid state physicists, there is only one general conclusion to be drawn from the data. It was mentioned in Chapter I that there had been some question about the oxygen-to-tungsten ratio of bronzes. These data support the idea that the bronzes have an oxygen-to-tungsten ratio of 3.000; lithium bronzes may be an exception. Tables 15 and 16 are the compilation of the bronze data.

C. Conclusions and Recommendations

In general, hydrogen and bromine trifluoride have been valuable and dependable reagents for the analysis of alkali metal tungstates and bronzes and of tungsten oxide. The methods gave good accuracy and precision. The lithium compounds were more difficult (133) to decompose by both reagents and forced the use of a different method for determining tungsten in combination with lithium. Perhaps, someone should study the chemical properties of lithium bronzes and tungstates in more detail with the object of improving the analyses.

There were no interferences with the methods used in this research. However, there may arise an application which is more complicated. For example, mixed bronzes of potassium and sodium have been prepared. In a case of this sort, flame photometry might be the best means of determining the individual alkali metals. Of the elements which were not studied in this research, some have volatile fluorides and some do not. The lists compiled by Yost and Russell (146) and by Weinstock (142, pp. 125-129) are helpful in assessing the volatility of fluorides and their possible interference or utility in the bromine trifluoride method. It was not necessary to investigate other applications of and the interferences to the nitric acid-hydrogen peroxide and hydrogen reduction methods.

These three methods, or modifications thereof, should be useful for analyses of many types of materials. One might apply them to the bronzes of molybdenum, niobium, tantalum, titanium, vanadium, and the non-alkali metal bronzes of tungsten. The methods should be capable of analyzing many kinds of oxysalts like molybdates, niobates, etc. They probably can be applied to the analysis of many oxides and other materials. However, these ideas are speculative and will have to be tested.

The vacuum system, which was constructed for performing the fluorinations and oxygen measurements, has operated tolerably well. But there are a few improvements which ought to be attempted. The priority item must be obtaining a more rapid transfer of bromine trifluoride from one container to another; transfer of the reagent has generally been quite slow. Larger bore tubing, shorter transfer routes, and better design of traps and still columns could be ways of improving the transfer rate. Another problem was the flanges on the still pots. The Kel-F tubes have small flanges molded on them and these are sometimes squeezed off by the metal flanges which seal the pots onto the still columns. Because the Kel-F tubes are expensive, an improvement here would be economical. The diffusion pump did not contribute anything significant to the operation of the system and ought to be removed. More efficient trapping of fluoride compounds should be introduced between the reactor vessel and the oxygen measuring subsystem. Otherwise, a periodic cleaning of the Töpler pump, transfer manometer, and the associated tubing is necessary. Finally, a clever designer might be able to simplify the whole apparatus and reduce its overall size.

Table 13. Summary of analytical data for tungsten trioxide

	WO_3 (Raby)	WO_3 (Fisher)	WO_3 (VarLacOid)	WO_3 (Amend)	WO_3 (North)
% Oxygen (theory)	20.70				
% Oxygen (found)	20.71±0.15				
% Tungsten (theory)	79.30	79.30	79.30	79.30	79.30
% Tungsten (found)	79.32±0.03	79.30±0.13	79.28±0.08	79.21±0.10	79.12±0.35
Oxygen-to-tungsten ratio	3.000	3.005	3.004	3.016	3.033
% Summation	100.03				

Table 14. Summary of analytical data for tungstates

	Li_2WO_4 (G-S)	Na_2WO_4 (Baker)	K_2WO_4 (McKay)	$Rb_6W_6O_{21}$ (Raby)	Cs_2WO_4 (G-S)
% Metal (theory)	5.30	15.65	23.98	26.27	
% Metal (found)	4.97±0.05	15.66±0.04	24.02±0.04	25.15	
% Oxygen (theory)	24.45	21.77	19.63		
% Oxygen (found)	26.86±0.11	21.84±0.05	19.63±0.09		
% Tungsten (theory)	70.24	62.57	56.39	56.51	35.79
% Tungsten (found)	68.15±0.16	62.50±0.25	56.34±0.05	55.93±0.46	35.75±0.14
Metal-to-tungsten ratio	1.932	2.004	2.003		
Oxygen-to-tungsten ratio	4.529	4.018	4.002		
% Summation	99.98	100.00	99.99		

Table 15. Summary of analytical data for bronzes

Number	Bronze specimen	Metal	Color
1	Na-1	Na	red
2	Na-2	Na	brass
3	Na-3	Na	red
4	Y-2	Na	orange
5	235-I	Na	red
6	236-A	Na	yellow
7	352b	Na	blue
8	352d	Na	dark blue
9	DCL-14-15F	Na	dark red
10	235P-C-1	Na	red
11	235P-C-2	Na	red gray
12	Li-1	Li	gray green
13	K-1A	K	blue
14	K-2A	K	blue

Table 16. Summary of analytical data for bronzes

No.	% metal	% tungsten	% oxygen	Metal-to-tungsten ratio from hydrogen reduction	Metal-to-tungsten ratio from total analysis	Oxygen-to-tungsten ratio	Summation of %
1	5.47±0.53	75.06±0.10	19.58±0.34	0.578	0.582	2.997	100.11
2	7.42±0.14	73.54±0.04	19.24±0.16	0.789	0.807	3.006	100.20
3	5.88	74.60±0.40		0.636	0.632	3.007	100
4	5.12±0.09	75.16±0.09	19.69±0.21	0.556	0.545	3.010	99.97
5	5.80±0.10	74.64±0.51	19.52±0.25	0.630	0.621	3.005	99.96
6	8.18±0.24	72.85±0.06	19.25±0.79	0.892	0.898	3.036	100.36
7	3.67±0.22	76.39±0.15	20.00±0.25	0.386	0.384	3.008	100.06
8		74.60±0.37		0.636			
9		75.66±0.17		0.484			
10		74.62±0.10		0.634			
11		75.16±0.20		0.556			
12	0.75±0.16	77.50±0.04	21.71±0.51	0.777	0.256	3.219	99.96
13		75.50±0.12		0.300			
14		75.36±0.15		0.311			

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