AN ABSTRACT OF THE THESIS OF

Richard Theodore VanSanten for the _____ M. S. _____
     (Name of student)   (Degree)

in _____ Chemistry _____ presented on December 16, 1966
          (Major)   (Date)

Title: THE ANALYTICAL APPLICATION OF THE GALVANIC

DISSOLUTION OF NIOBIUM AND TANTALUM. THE

DETERMINATION OF NITROGEN

Redacted for Privacy

Abstract approved: _____
                               Dr. Harry Freund

Nitrogen is a contaminant of niobium and tantalum adversely affecting the workability of the metal. With recent interest in the refractory metals, one problem the chemical analyst must solve is the accurate determination of nitrogen in niobium and tantalum at very low levels. The usual method of assaying for nitrogen in metals uses a modification of the Kjeldahl fixation with subsequent distillation of the ammonia. The dissolution of niobium and tantalum was studied to elucidate a method in which a quantitative recovery of nitrogen could be attained in an economical period of time. Galvanic coupling of the sample with a more noble metal was found to increase the dissolution rates several fold. Methods using rhodium and osmium salts with tantalum and rhodium and platinum salts with niobium were developed using in situ coupling for more efficient

contact. The proposed methods were checked against "standard" procedures, and against a recent method using iodate and hydro-fluoric acid to promote dissolution.

The Analytical Application of the Galvanic
Dissolution of Niobium and Tantalum
The Determination of Nitrogen

by

Richard Theodore VanSanten

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1967

APPROVED:

Redacted for Privacy

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Date thesis is presented _December 14, 1966_

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INTRODUCTION

With the increasing interest and progress in aerospace and

nuclear technology comes a need for ever increasing high-strength

metals and alloys. During the late 1950's and early sixties the high-

strength at high-temperature properties of niobium and tantalum

captured many investigators' imagination. Programs were initiated

to develop and improve these metals by improving purity and by

alloying. Niobium is a good structural material for use in the range

of 1000 to 1400° centigrade (6, p. 85-115). When quite pure, it is

ductile, weldable, fabricates easily at room temperature, and is

more economically produced than tantalum. An added advantage is

the high melting point of its oxide, Nb_2O_5, 1499° centigrade in con-

trast to the oxide of molybdenum, MoO_3, 793° centigrade. Nitrogen

is a contaminant affecting the workability of the metal. The nitrogen

content of high purity niobium and tantalum is usually less than 0.02

percent and may be as low as 0.001 percent. The usual method of

determining nitrogen in niobium and tantalum is by a Kjeldahl pro-

cedure although some have suggested vacuum-fusion or inert-gas-

fusion methods (19).

The discovery, in 1883, usually attributed to Kjeldahl, that

boiling many nitrogen-containing organic compounds in concentrated sulfuric acid liberates the nitrogen as ammonium sulfate, is probably one of the most significant analytical discoveries made. The Kjeldahl procedure and its variations have been applied to every possible form of nitrogen in probably more laboratories than almost any other type of analytical method. The method was first used in the analysis of protein nitrogen and later extended to other nitrogen containing samples. Yet in the 80 odd years since Kjeldahl described his procedure, some of the greatest difficulties in the analysis of protein nitrogen remain unsolved. Quite naturally, when this concept was extended to analyzing metals for nitrogen, these problems carried over to the new application.

One of these problems is that acid decomposition will not fix nitrogen that is adsorbed on the surface or in the pores of the sample. Nitrogen which is present as a nitride or in solid solution, upon acid attack is liberated in the atomic state and is reduced or fixed as ammonia in the presence of liberated hydrogen. According to Turovtseva and Kunin (22, p. 207), most of the nitrogen present in metals is present as nitride and is amenable to acid attack. The solution of nitrides is actually an oxidation-reduction process. Due to the copious evolution of hydrogen, the oxidation of nitrogen is not favored and the nitrogen, liberated in the atomic form, reacts with the excess of hydrogen formed during dissolution of the metal.

The solution of a metal containing only soluble nitrides is therefore straightforward. The problems mount with metals which form insoluble or only partially soluble nitrides, or with metals which themselves are difficultly soluble in the acids normally used (hydrochloric, sulfuric, and sometimes perchloric acids). This group includes the elements of Groups IVB, VB, and VIB. Metal containing large amounts of carbon is also difficult to dissolve because of the very stable carbonitrides present.

KJELDAHL DETERMINATIONS IN METALS

The first application of a Kjeldahl method to metal occurred when the metallurgically deleterious effects of nitrogen in steel were realized. A. H. Allen first published a method later modified by Professor J. W. Langley (8, p. 770-772) in which the sample is dissolved in hydrochloric acid and then distilled in the conventional way from a solution containing an excess of prepurified sodium sodium hydroxide. The ammonia distillate is collected in a known amount of standard sulfuric acid, followed by titration with standard acid and/or base. The insoluble nitrides were judged to decompose during distillation, although this probably occurred only when very high (up to 60 percent) concentrations of caustic were used. Present day practice (2, p. 66-68) remains substantially the same, with the additional use of selenium as a catalyst and the use of different acids when refractory impurities are present.

Because of the severe effects of nitrogen on the ductility and corrosion of Group IVB metals, it was necessary to determine nitrogen accurately at low levels. In 1959 the American Society for Testing and Materials agreed on a standard method (1, p. 549-552) for determining nitrogen in zirconium by a Kjeldahl-like procedure. The sample was dissolved in hydrochloric-hydrofluoric acid solution, after which the solution was made basic with sodium hydroxide and

the nitrogen separated as ammonia by steam distillation. The dis-
tillate was collected in water and Nessler's reagent added to form
the yellow amine complex. Photometric measurement was made
at 430 millimicrons.

In 1960, ASTM (1, p. 503-505) published a similar method
for nitrogen in titanium. The sample was dissolved in fluoboric-
hydrochloric acid solution, the distillate collected in one percent
boric acid solution, followed by titration with standard acid.

In 1961, ASTM (2) adopted a method for nitrogen in niobium
in which the sample was dissolved in hydrofluoric-hydrochloric acid
solution in a platinum vessel at a temperature of 90 to 95° centi-
grade using hydrogen peroxide to initiate the reaction. A 1/10 ali-
quot of the sample was made basic with prepurified sodium hydrox-
ide and the nitrogen separated as ammonia by steam distillation.
The procedure was finished by "Nesslerization" as described in the
ASTM method for zirconium. This is similar to method described
by Mallet and Harris (21, p. 3; 12, p. 76-95). Mallet specified
dissolving a 0.5 gram sample of niobium, tantalum, or tungsten in
five milliliters of 1:1 sulfuric acid, two milliliters 48 percent hydro-
fluoric acid and one milliliter hydrogen peroxide in a platinum ves-
sel, after which the sample was evaporated to white dense fumes
prior to distillation. The purpose of fuming is two-fold. Hydrogen
peroxide must be removed for if any remains during distillation

foaming with a resultant carryover of sodium hydroxide aerosol would occur. Also fuming reduces the amount of acid thus permitting the use of the complete sample. Mallet finished his procedure either titrimetrically or photometrically with the use of Nessler's reagent.

An interesting method has been suggested by Harris (12, p. 57; 19) in which the sample is dissolved and the nitrogen fixed and evolved as ammonia simultaneously from an alkali-fusion. The fusion apparatus consisted of a Vycor tube 30 inches long and 1-1/4 inches in diameter, fitted with ground glass joints at each end and tubes for the passage of carrier gas. A nickel boat containing sodium hydroxide and the sample is placed inside a nickel sleeve which protects the combustion tube from spattered alkali. The mixture is heated with a 12 inch split tube furnace at 600° centigrade up to an hour in a slow stream of hydrogen. This method was applied to beryllium, molybdenum, tungsten, niobium, and tantalum. One problem which arises is the failure to recover quantitatively nitrogen associated with impurities such as zirconium, hafnium, iron, etc.

The dissolution of niobium by heating in a sulfuric acid-potassium pyrosulfate mixture is used by several laboratories (20, p. 76-95; 21; 24). A one gram sample is weighed into a Kjeldahl flask and about five to ten grams of potassium pyrosulfate and ten to 20 milliliters of concentrated sulfuric acid are added. The mixture is fused to a clear solution, cooled, diluted, and distilled in either a

conventional manner or by steam distillation followed either by titration or the use of Nessler's reagent. While this technique appears successful, Kirk (15) notes that precautions to maintain an excess of sulfuric acid are necessary to prevent loss of nitrogen during the digestion. He attributes the loss to the fact that elemental nitrogen is slightly more stable than ammonia, and that any oxidizing condition might lead to a partial oxidation of ammonia to nitrogen. The fact that sulfuric acid is so mild an oxidizing agent has permitted its use as a general solvent for Kjeldahl determinations (15).

All of the above methods for dissolution of tantalum and especially niobium have a common failing. The reaction proceeds so slowly that either finely-divided samples must be used or long dissolution times employed, with consequent ammonia pickup from the atmosphere. As ammonia is a common reagent in use in most laboratories, this becomes a significant and serious problem. Either the laboratory used for nitrogen analyses must be separated from areas where ammonia is in use or the room must be well sealed with any incoming air purified to remove atmospheric ammonia. As both tantalum and niobium metals are active and react with atmospheric nitrogen on long exposure, the use of finely divided samples is not attractive. Solid (or massive) samples, on the other hand, are not dissolved rapidly enough by conventional

methods to be certain that atmospheric contamination by ammonia does not occur, even with efficient isolation of the laboratory and efficient pruification of incoming air.

Very recently, Jaworowski (13) proposed a rapid dissolution of niobium and tantalum with hydrofluoric acid in the presence of potassium iodate, which is suitable in preparation for nitrogen analyses.

Unfortunately, the dissolution of niobium, and to some extent tantalum, for purposes of analyzing the nitrogen content presents a dilemma. While ordinarily an oxidizing agent such as nitric acid is used with hydrofluoric acid, to prevent passivation of the surface of metallic niobium or tantalum, one should also provide reducing conditions to insure reduction of nitrogen to NH_4^+.

It is routine practice in the author's laboratory to add hydrofluoric acid to cover a sample, and then to add nitric acid dropwise to dissolve the sample rapidly. During the routine dissolution of a rhodium-containing niobium alloy, it was noted that an extremely fast reaction occurred prior to the addition of nitric acid. As a matter of fact most of the sample and solution was deposited on the ceiling of the hood. As the phenomenon appeared to be similar to that of the well known (9) increase in dissolution rate of tin when galvanically coupled with platinum, a literature search was initiated to survey the present status of knowledge regarding mechanism for dissolving metals.

ASPECTS OF CORROSION

The process of dissolving a metal sample in preparation for analysis is a corrosion process. The analytical chemist desires to accelerate the corrosion in order to complete the analysis within a reasonable period of time. The corrosion engineer, on the other hand, usually desires to inhibit dissolution or to sacrifice a base metal for an expensive metal. Various speculations have been made on the mechanism of corrosion. Some of the early investigators felt that certain types of corrosion, such as the tarnishing of silver or high-temperature air oxidation, was diffusion controlled (17, p. 37). Present day theory is based almost universally upon electro-chemistry (4;17;23).

In the book by LaQue and Copson (17, p. 7-37) corrosion is categorized into major descriptive types. Uniform attack is self-descriptive and quite rare, being typified by some examples of air oxidation and static solution. Pitting is characteristic of corrosion in solution by turbulent erosion, and by crevice or intergranular attack. Mechanisms described employ concentration cells, where a difference exists in the concentration in electrolyte at cathodic and anodic areas. Two main types are apparent. The "Metal-Ion Cell" has two pieces of the same metal immersed in separate solutions of differing concentration, developing a difference in potential.

When the metal is shorted and solutions connected, current will flow and corrosion occurs.

In the "Differential-Aeration Cell," areas exposed to high oxygen concentrations become anodic. This form occurs commonly in crevices. A variation of this cell is the "Passive-Active Cell." In this, the action of oxygen passivates or effectively forms a protective oxide film to form on some metals causing the surface to take on more noble-metal-like characteristics, whereas areas shielded from oxygen remain or become active.

Commercial metals are never homogenous. For instance, gray iron contains graphite. In certain media such as brines and mild acids, iron corrodes while the graphite remains in place unchanged. Even iron carbides show a similar noble characteristic. Some corrosion occurs at the grain boundary, caused by a difference in potential between the grain boundaries and the grain. Galvanic corrosion is commonly seen in protecting valuable bronze and steel parts of ships by placing, and so sacrificing, zinc or magnesium plates in intimate contact with the parts to be preserved and the water.

Present day theory then can be summed as follows (17, p. 83-104): Most metals exist in nature in the combined state. Their ores or natural compounds must be subjected to pyro-metallurgical and chemical refining processes involving an addition of energy to bring

them to the metallic state. It follows that the natural tendency of metals is to combine with other substances and to revert to a lower energy state. This decrease in free energy is the driving force of corrosion reactions. Corrosion is usually electrochemical in nature and is the basis for the use of couples to protect a more valuable metal in solution.

Even high temperature direct oxidation has been described as electrical in nature. It was once thought to be a direct chemical reaction controlled by simple diffusion of the reactant atoms. Based largely on work by Wagner, experiment has shown that reaction may occur by metal ions diffusing outward through the corrosion product film accompanied by a flow of electrons. There may also be some diffusion of reactant ions inward. The film thus acts as both the internal and external circuits of a closed cell.

Buck and Leidheiser (4;5) and Kolotyrin (16), investigating the corrosion of various base metals found that the addition of various noble metal ions accelerated corrosion of the base metal. Buck and Leidheiser found that some metals were more effective than others in catalyzing dissolution, and described five types of behavior: (a) Activation of the cathodic reaction; (b) activation of the anodic reaction; (c) inhibition of the anodic reaction; (d) inhibition of the cathodic reaction; and (e) inhibition of both the anodic and cathodic reaction. They followed the reactions by both externally coupled

electrodes and by adding the extraneous metal ions in solution. In the latter case they noted a plating of some of the noble metals on the surface of the base metal almost immediately after addition with a subsequent increase in evolution of gas and corrosion rate of tin and iron. In their studies of titanium (4), they found that Group VIII metals inhibited solution in two molar hydrochloric acid. Again, the corrosion rate was affected only after the added metal plated out on the surface of the base metal. The corrosion rate was thought to be dependent on the type of bond between the metals: Covalency causes lower reactivity, ionic bonds higher or lower depending on the relative orientation of the positive and negative charges.

The electrochemical kinetics of a cell can be described as being controlled by four factors (7, p. 1021): (a) The ohmic drop through the cell is obviously diminished by bringing the electrodes closer together. (b) Concentration polarization occurs when, as current flows, the concentration near the anode and/or cathode changes. Any such change tends to oppose further flow of current. This can be prevented, or at least minimized, by vigorous stirring. (c) Approach-resistance polarization occurs when a deposit is formed on one of the electrodes, with crystals forming with decreasing frontal area. As these crystals continue to form at the preferred face, resistance to current flow increases because of the diminishing area available for further electrochemical reaction. (d) So long as

no net current flows in a half-cell between the anode and solution,

the potential must be such that the left-to-right reaction exactly

balances the right-to left reaction

$$M \rightleftharpoons M^{n+} + n(e)$$
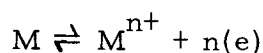
If current is to flow, then at the anode the left-to right reaction must

exceed the right to left reaction, and this requires a displacement of

the potential in the positive direction. The same sort of criteria

apply to the cathode. At a "normal" electrode such as silver, the

activation polarization (the difference in potential between the condi-

tion of no current flow and current flow) is relatively small. For

"abnormal" or transition metals such as iron and nickel, it may be

quite large. It is extremely large for the cathodic evolution of hydro-

gen on certain surfaces, in which case this polarization is generally

known as overvoltage. The activation polarization can be expressed

by the equation

$$I = Ke^{-(w+ne)(1-\alpha)(V+\Delta V)/kT}$$

at each electrode where α is V_1/V and ΔV is the departure of poten-

tial from equilibrium. The current flowing in each direction in a cell

under equilibrium conditions ($\Delta V = 0$) is known as the exchange cur-

rent, I_o, and the corresponding current density, I_o/A, is written

as i_o. The curve relating the net current density, i, with the depar-

ture ΔV from the equilibrium potential is the difference between two

exponentials (from the above equation). At a sufficient ΔV, one exponential becomes small compared with the other, and then the net current density can be written with sufficient accuracy by the single term on the right of the above equation. Then

$$\log_e(i/i_o) = n\varepsilon\alpha\ \Delta V/kT$$

or

$$V = \frac{kT}{h}\log_e\frac{i}{i_o} = b\log_{10}\frac{i}{i_o}$$

This is often written $V = a + b\log_{10}i$ and is known as Tafel's equation, with b called the Tafel slope. Tafel's relation between log i and V is only true if complicating factors such as concentration polarization are absent.

Buck and Leidheiser (4;5) showed a correlation between V and log i in their work with 15 cations in solution with iron, tin, and lead with a Tafel slope corresponding in most cases with the electron change.

The ordinary method (7, p. 1023) of measuring the potential for Tafel's equation is by placing a tubulus with the opening close to the electrode surface and connecting, through a suitable salt bridge, to a reference electrode. In some work (4;5) this has been dispensed with, the measurement being made directly in the solution media.

It is of interest to note that a patent has been granted for coupling by alloy addition of platinum to uranium base molybdenum

and/or niobium alloys (18) to increase resistance to corrosion.

Since the purpose of this investigation was to improve the efficiency of dissolving niobium and tantalum in preparation for analysis, the experimental effort was directed at developing a better solution method and not to dwell on the mechanisms involved.

EXPERIMENTAL

Reagents and Materials

(1) Niobium: 1/4 inch rod; 120 micron foil; minus 100 mesh powder (Wah Chang Corporation, Albany, Oregon).

(2) Tantalum: 1/4 inch rod; 63 micron foil; minus 200 mesh powder (Wah Chang Corporation, Albany, Oregon).

(3) Platinum: Minus 325 mesh powder reduced by thermal decomposition of ammonium chloro platinate.

(4) Rhodium: Minus 325 mesh powder; rhodium chloride tetra-hydrate (J. Bishop and Company, Malvern, Pennsylvania).

(5) Ruthenium, Palladium, Osmium, and Iridium: Minus 325 mesh powders (Engelhard Industries, Incorporated, Newark, New Jersey).

(6) Noble metal solutions: The noble or platinum metals were dissolved without the introduction of nitric acid, following the method of Wichers, Schlect, and Gordon (10;25).

Heavy wall eight millimeter Pyrex manometer tubing was cut in approximately ten inch lengths and one end sealed in the gas-oxygen flame and well worked to provide a smooth strong hemis-pherical end. Approximately 0.3 gram of metal was weighed into the tube, and about one gram of anhydrous sodium perchlorate added.

The closed end of the tube was immersed in a dry-ice acetone bath. Approximately two milliliters of 37 percent hydrochloric acid was added to the tube and frozen.

A steel bomb, approximately one inch inside diameter by 12 inches long with a one inch thick wall and with Teflon gaskets and threaded ends and caps was prepared. One end was screwed on and tightened with a wrench. About five grams of calcium carbonate was added and a glass wool plug inserted into the bomb. The lime was used in case of a rupture of the glass tube so that the acid released could be absorbed before it could attack the steel and evolve large amounts of hydrogen.

The glass tube was then inserted into the steel bomb, about one gram of solid carbon dioxide added to prepressurize the bomb and effectively lower the pressure differential on the glass tube at the reaction temperature. A glass wool plug was inserted and the remaining Teflon gasket and cap screwed on quickly and tightened with a wrench. The assembled bomb was checked for gas-tightness by immersing in water. Upon confirmation of a secure bomb, it was placed in a muffle and heated to 300° centigrade. According to the original work, the pressure developed inside the glass tube under these conditions approximated 400 p.s.i.

After the reaction proceeded overnight, the bomb was removed from the muffle and allowed to cool to room temperature, at which

time it was opened and the glass tube, if still intact, quickly im-
mersed in the dry-ice acetone and the solution frozen.

The glass vial was opened by heating with a small gas-oxygen
flame until a small hole was blown out by the chlorine gas under
pressure inside. The opened end was pulled out to a narrow neck
which was broken off. The vial was inverted into the neck of a
volumetric flask to drain. The vial was broken in two near the
bottom and rinsed into the flask, and the solution brought to the
mark with water. In the case of ruthenium and osmium the solu-
tions were diluted with four molar hydrochloric acid to prevent
hydrolysis.

(7) Hydrofluoric acid, 48 percent, Electronic (Baker and
Adamson).

(8) Hydrogen peroxide, 30 percent, Reagent (J. T. Baker).

(9) Sulfuric acid, Concentrated, Reagent (Baker and Adamson).

Apparatus

(1) Hot water bath-shaker (Research Specialties Company).

(2) Teflon beakers, 150 milliliter.

(3) Noble metal electrodes: Electrodes were fabricated from
the minus 325 mesh powders by pressing in a 1/4 inch diameter
Stokes press and sintered at approximately 1500° centigrade in a
Laboratory Equipment Company No. 523 induction furnace under an

atmosphere of argon. Pellets so formed were pressed into 1/4

inch i. d. polyethylene tubing leaving only one face exposed. The

surface was faced with fine grit silicon carbide paper.

(4) Group V metal electrodes: 1/4 inch niobium and tantalum

rods were pressed into polyethylene tubing as above, and the surface

dressed with fine grit silicon carbide paper.

<div align="center">Experimental Procedure</div>

The noble metal electrodes were connected in turn with the

niobium and tantalum electrodes and placed approximately 1.0

centimeter apart in the circuit shown in Figure 1. They were im-

mersed in a plastic beaker containing 48 percent hydrofluoric acid

held at 70° centigrade and agitated by a gentle transverse motion.

The results are shown in Table 1. The potential vs. saturated

calomel electrode was -0.44 and -0.54 volts respectively for

niobium and tantalum, as measured with a vacuum tube voltmeter.

Replicate potentials were reproducible within ten millivolts.

Following this experiment, the six "platinum" metal chloride

solutions were made 2×10^{-3} molar in 48 percent hydrofluoric acid.

One centimeter squares of niobium and tantalum foil were dissolved

in the mixtures thermostated at 70° centigrade and agitated with

gentle transverse motion. The lengths of time taken for dissolution

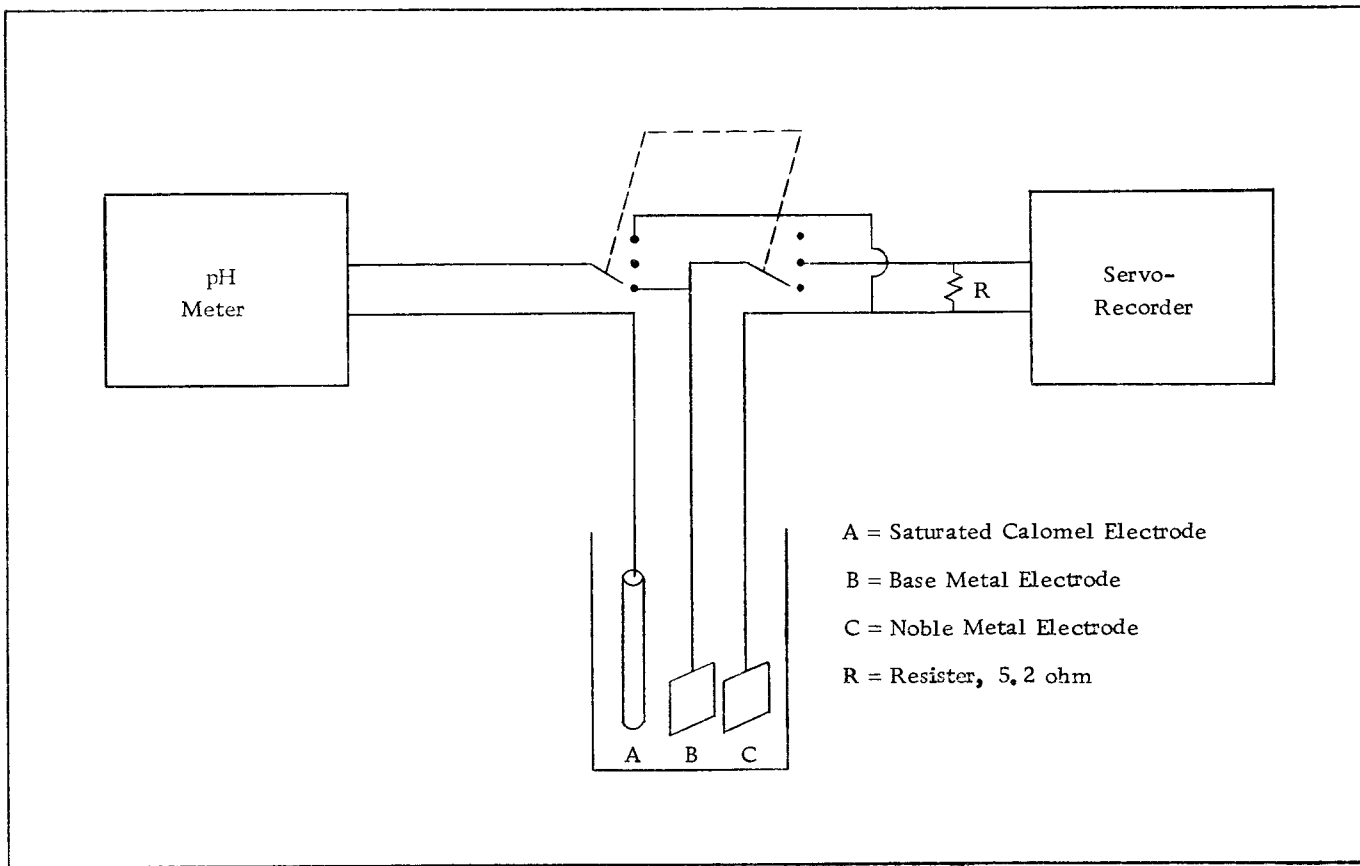are listed in Table 2. In addition, the 1/4 inch diameter electrodes

Figure 1. Circuit for following galvanic couples

A = Saturated Calomel Electrode

B = Base Metal Electrode

C = Noble Metal Electrode

R = Resister, 5.2 ohm

Table 1. Galvanic couples with niobium and tantalum. Electrodes:
1 cm. apart.

Noble metal electrode	Current, ma. per cm^2	
	Nb	Ta
Ruthenium	788	884
Rhodium	350	533
Palladium	169	153
Osmium	336	486
Iridium	nil	nil
Platinum	576	938

Table 2. Galvanic dissolution of niobium and tantalum by
precipitation- coupling with noble metals.

Metal added 2×10^{-3} M in 48% hydrofluoric acid thickness	Dissolution time, minutes		Dissolution rate, mg. /cm.^{2}/hr.	
	Nb 120µ	Ta 63µ	Nb	Ta
Ruthenium	224	3.83	13.8	819
Rhodium	840	1.08	3.7	2905
Palladium	1700	2.33	1.8	1350
Osmium	38	67	81	47
Iridium	505	5.67	6.1	553
Platinum	12	18.5	257	170
None	2800	62	1.1	51

were immersed in the six "platinum" metal chloride solutions therm-

stated at 70° centigrade and the potential measured vs. SCE. These

results are shown in Table 3 and in Figures 2 and 3.

Table 3. Potential developed during precipitation-coupling of
niobium and tantalum with noble metals.

Metal added 2 × 10⁻³ M in 48% hydrofluoric acid	Potential at 70° C versus SCE, mv	
	Nb	Ta
Ruthenium	-390	-400
Rhodium	-365	-375
Palladium	-400	-433
Osmium	-433	-537
Iridium	-418	-470
Platinum	-375	-340
None	-436	-536

Metal added column header reads 2×10^{-3} M in 48% hydrofluoric acid.

Next a similar experiment was performed using additions of

compounds which might aid in complexing the two earth acid elements.

These included sulfuric, oxalic, tartaric, and citric acids, and hy-

drogen peroxide. Only the latter gave positive results. These data

are shown in Table 4, including additions of two noble metals at a

time. In the case of hydrogen peroxide additions, the "platinum"

metal first precipitated on the base metal and then immediately

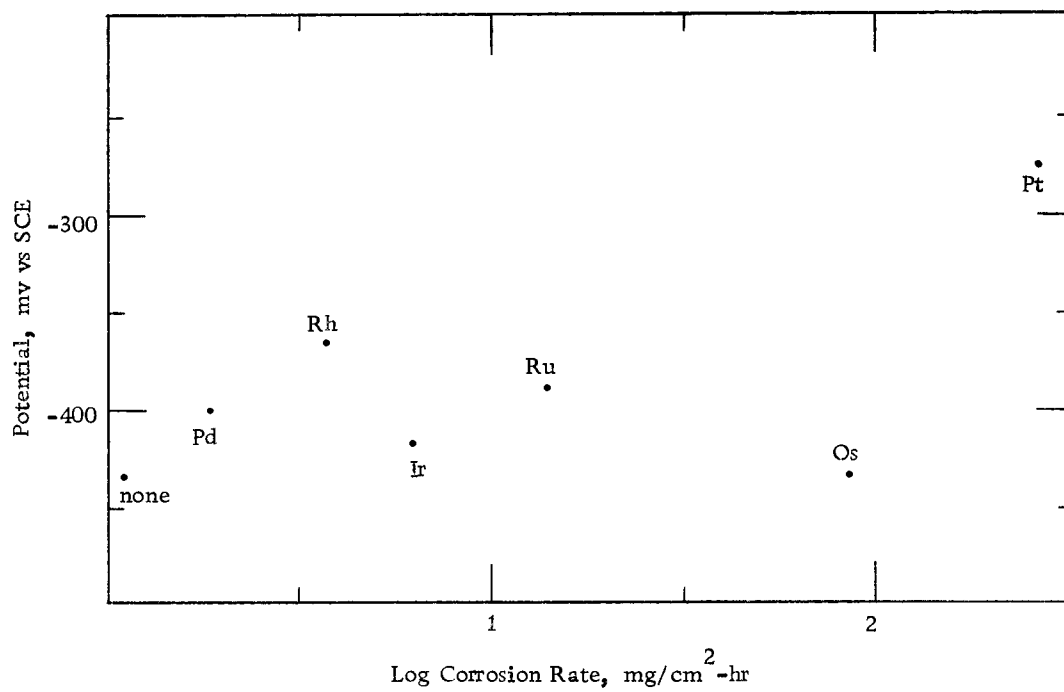started redissolving with no apparent change in rate of dissolution

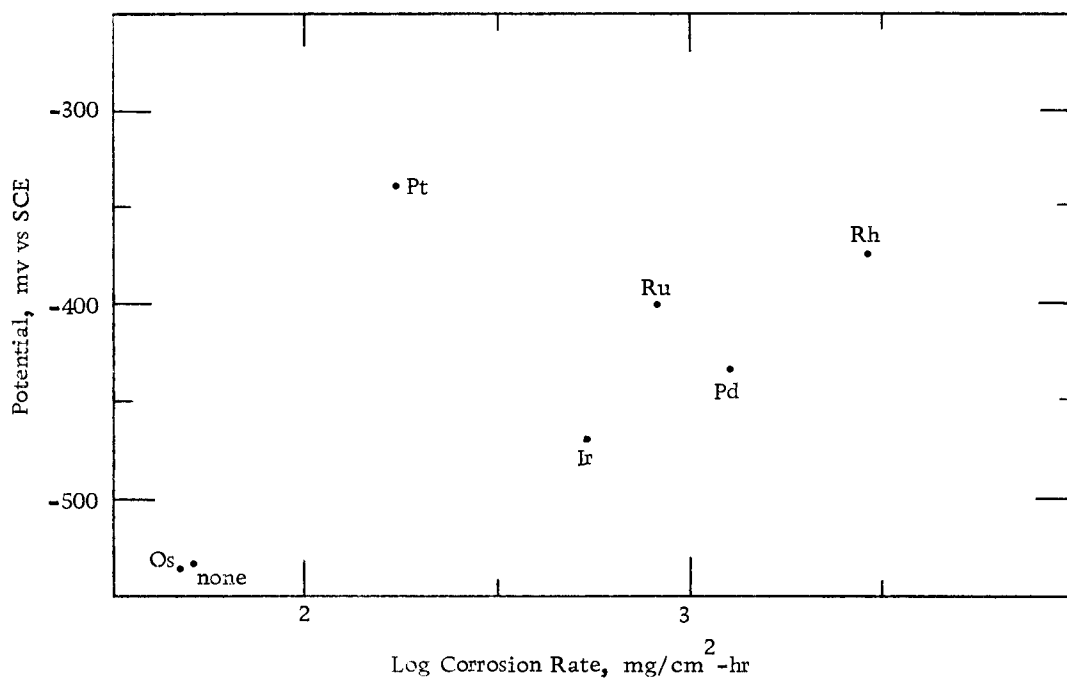Figure 2. Corrosion of niobium in hydrofluoric acid

Figure 3. Corrosion of tantalum in hydrofluoric acid

of the base metal.

Table 4. Galvanic dissolution of niobium and tantalum by precipita-
tion-coupling of rhodium, osmium, and platinum in the
presence of hydrogen peroxide.

Metal added $2 \times 10^{-3}\underline{M}$ in 43% hydrofluoric acid, 3% hydrogen peroxide	Dissolution rate, mg. /cm.^{2}/hr.	
	Nb	Ta
Rhodium	1910	6270
Osmium	1	314
Platinum	2150	3420
Rhodium/Osmium	1140	9410
Rhodium/Platinum	5790	8960
Osmium/Platinum	916	4950
None	$\ll 1$	216

RECOMMENDED PROCEDURE

Tantalum

Reagents

(1) Hydrofluoric acid, 48 percent, electronic.

(2) Osmium chloride, nitrogen free, 0.3 percent.

(3) Rhodium chloride, nitrogen free, 0.6 percent.

(4) Sodium hydroxide, 50 percent, reagent.

(5) Hydrochloric acid, 0.00357 molar.

(6) Boric acid, reagent, 0.2 percent.

(7) Mixed indicator (Dissolve 0.1 gram brom cresol green in 50 milliliters ethanol. Dissolve 0.07 gram methyl red in 70 milliliters ethanol. Mix.)

Note: All water used in analysis is >50,000 ohm--cm. ion-exchange water.

Apparatus

(1) Teflon beakers, 150 milliliter with covers.

(2) Hot water bath-shaker.

(3) Auto-pipet, ten milliliter.

(4) Kjeldahl semi-micro steam distillation apparatus (American Instrument Company, Silver Spring, Maryland, as modified per

Figure 4).

(5) Buret, ten milliliter.

Method

Samples are treated in one of two ways depending upon physical form:

If solid or massive specimens are to be analyzed, first rinse approximately a one gram piece with five percent hydrofluoric acid followed by a water rinse and an acetone rinse. Immediately weigh accurately and place in a Teflon beaker containing ten milliliters of hydrofluoric acid and five drops each of osmium and rhodium solutions.

If a powder or fine turning specimen is analyzed the washing procedure is omitted.

Place in the hot water bath-shaker at 70° centigrade, cover, and agitate until solution is complete. Clean the distillation apparatus by steam distilling 50 percent sodium hydroxide and flushing well with ion-exchange water. Cool and quantitatively transfer the solution to the distillation flask. Add ten milliliters of boric acid from the Auto-pipet to a 125 milliliter Erlenmeyer flask. Place under the condenser and add 40 milliliters of 50 percent sodium hydroxide to the distillation flask. Insert the steam supply tube and steam distill until 30 to 40 milliliters of distillate is collected.
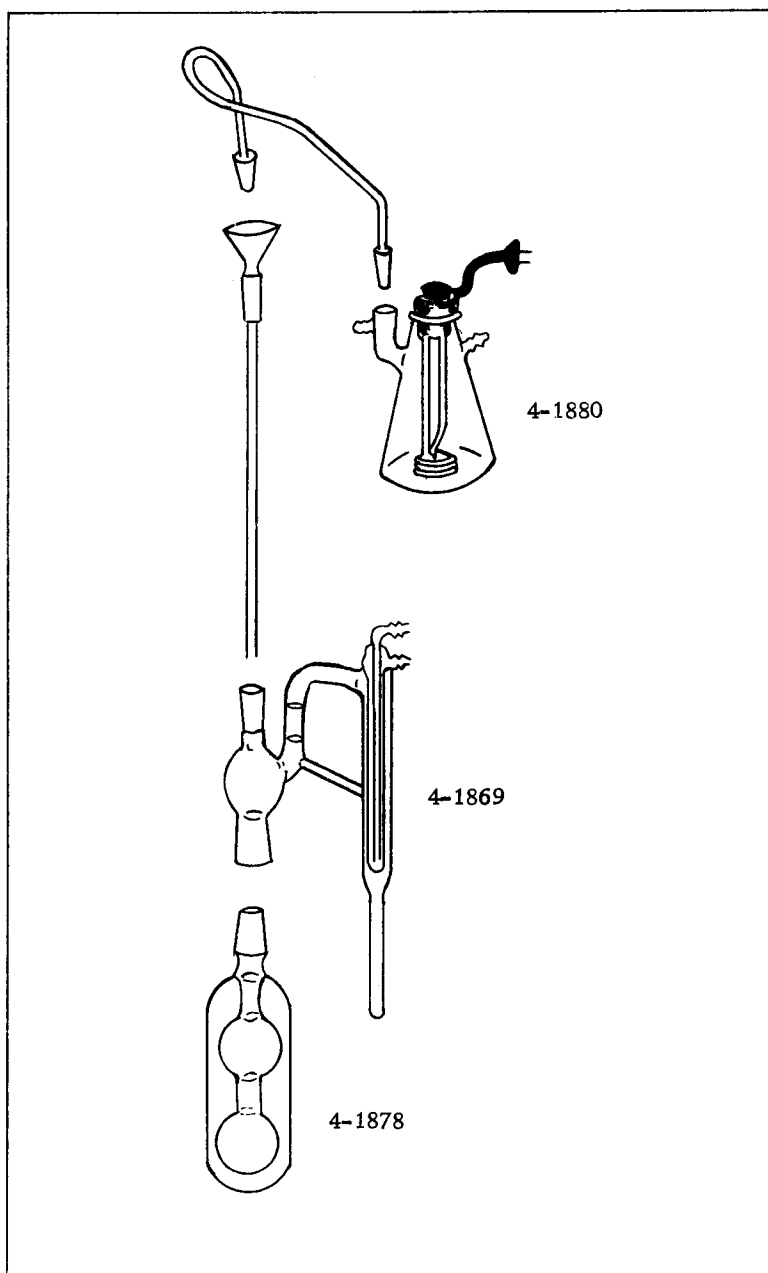
4-1880

4-1869

4-1878

Figure 4. AMINCO semi-micro Kjeldahl steam
distillation unit, modified

Titrate with standard hydrochloric acid to the pink end point. Carry a reagent blank through the procedure.

Calculate nitrogen content as: $\text{ppm} = \dfrac{(A-B)50}{C}$

where A = Hydrochloric acid titration, milliliters,

B = Blank titration, milliliters,

and C = Sample weight, grams.

Niobium

Reagents

(1) Hydrofluoric acid, 48 percent, electronic.

(2) Platinum chloride, nitrogen free, 0.3 percent.

(3) Rhodium chloride, nitrogen free, 0.6 percent.

(4) Hydrogen peroxide, 30 percent, reagent.

(5) Sulfuric acid, concentrated, reagent.

(6) Sodium hydroxide, 50 percent, reagent.

(7) Hydrochloric acid, 0.00357 molar.

(8) Boric acid, reagent, 0.2 percent.

(9) Mixed indicator (Dissolve 0.1 gram brom cresol green in 50 milliliters ethanol. Dissolve 0.07 gram methyl red in 70 milliliters ethanol. Mix.)

Note: All water used in analysis is >50,000 ohm--cm. ion-exchange water.

Apparatus

(1) Teflon beakers, 150 milliliter with covers.

(2) Hot water bath-shaker.

(3) Auto-pipet, ten milliliters.

(4) Kjeldahl semi-micro steam distillation apparatus (American Instrument Company, Silver Spring, Maryland, as modified per Figure 4).

(5) Buret, ten milliliter.

Method

Samples are treated in one of two ways depending upon physical form:

If solid or massive specimens are to be analyzed, first rinse approximately a one gram piece with five percent hydrofluoric acid followed by a water rinse and an acetone rinse. Immediately weigh accurately and place in a teflon beaker containing ten milliliters of hydrofluoric acid and five drops each of osmium and rhodium solutions.

If a powder of fine turning specimen is to be analyzed the washing procedure is omitted.

Add 0.50 milliliter of hydrogen peroxide. Place in the hot water bath-shaker at 70° centigrade, cover, and agitate until

solution is complete. <u>Cool.</u> Add one milliliter of sulfuric acid and heat to dense fumes of SO_3. <u>Cool.</u> Clean the distillation apparatus by steam distilling 50 percent sodium hydroxide and flushing well with ion-exchange water. Quantitatively transfer the sample solution to the distillation flask. Place a 125 milliliter Erlenmeyer flask to which ten milliliters of boric acid have been added from the Auto-pipet under the condenser and add 40 milliliters of 50 percent sodium hydroxide to the distillation flask. Insert the steam supply tube and steam distill until 30 to 40 milliliters of distillate are collected. Titrate with standard hydrochloric acid to the pink end point. Carry a reagent blank containing about one gram of high purity tantalum foil through the procedure.

Calculate nitrogen content as: $\text{ppm} = \dfrac{(A-B)50}{C}$

where A = Hydrochloric acid titration, milliliters

B = Blank titration, milliliters

and C = Sample weight, grams.

RESULTS

Samples of tantalum were analyzed for nitrogen by the pro-cedure of Mallet (19), while samples of niobium were analyzed by the method of VanSanten and Valder (24). In addition Jaworowski's proposed procedure (13) as applied to niobium was compared with the pyrosulfate dissolution method. These procedures are given in detail in the Appendix. Metal powder samples were used to obviate segregation effects as much as possible. The results are shown in Tables 5, 6, and 7. The values for niobium are adjusted for the nitrogen contributed by the tantalum addition. In addition the sample of niobium was analyzed by the recommended procedure with the deletion of the use of hydrogen peroxide and of tantalum in the blank by weighing the samples and placing in polyethylene bottles, adding reagents, capping tightly and placing in the hot water bath until dissolution was complete. The results were: 202.3, 186.2, and 196.4 or 195.0 ppm ± 8.2 ppm.

Table 5. Comparison of proposed procedure to the procedure of Mallet in the determination of nitrogen in tantalum.

	"Mallet"		"Proposed"	
Blank, μg	Nitrogen, ppm		Blank, μg	Nitrogen, ppm
5.0, 4.0, 8.5	126.5, 132.5, 148.0 = 135.6		nil	108.0, 105.5, 101.0 = 106.8
4.0, 8.0, 6.0	124.0, 130.0, 134.5 = 129.5		nil	109.0, 104.5, 116.5 = 110.0
27.0, 16.0, 6.0	136.5, 131.0, 129.0 = 132.2		nil	113.0, 119.5, 116.5 = 116.3
17.0, 16.0, 17.5	110.5, 127.1, 122.2 = 119.9		nil	110.9, 110.0, 119.0 = 113.3
	Average:	129.3		Average: 111.6
	Standard deviation:	6.8		Standard deviation: 4.1

Table 6. Comparison of proposed procedure to the pyrosulfate procedure in the determination of nitrogen in niobium powder.

	"Pyrosulfate"			"Proposed"	
Blank, µg	Nitrogen, ppm		Blank, µg	Nitrogen, ppm	
nil	141.0, 149.5, 155.5 =	148.7	25.5, 31.5, 25.0	197.5, 226.5, 217.0 =	213.7
nil	135.5, 156.0, 164.0 =	151.8	26.0, 20.5, 11.5	179.0, 248.0, 226.0 =	217.6
nil	138.1, 151.4, 148.5 =	146.0	27.0, 22.5, 39.0	192.5, 186.4, 279.5 =	219.4
nil	140.9, 125.0, 143.3 =	136.4	63.0, 66.0, 67.0	192.1, 165.9, 182.2 =	180.1
	Average:	145.7		Average:	207.7
	Standard deviation:	6.6		Standard deviation:	18.6

Table 7. Comparison of Jaworowski's procedure to the pyrosulfate procedure in the determination of nitrogen in niobium millings.

|	"Pyrosulfate"		"Jaworowski"
Blank, μg	Nitrogen, ppm	Blank, μg	Nitrogen, ppm
5.0	45.0, 45.0, 47.5 = 45.8	7.5	57.5, 52.5, 58.0 = 56.0
5.0	42.5, 41.5, 46.0 = 43.3	7.5	56.0, 64.5, 68.0 = 62.8
5.0	42.5, 46.5, 50.0 = 46.3	5.0	57.5, 52.0, 53.0 = 54.2
7.5	35.0, 36.0, 46.5 = 39.2	5.0	55.0, 53.5, 57.5 = 55.3
	Average: 43.6		Average: 57.1
	Standard deviation: 3.2		Standard deviation: 3.9

DISCUSSION

The preliminary experiments leading to the recommended

procedures for dissolution of niobium and tantalum preparatory to

analysis for nitrogen were difficult to interpret. When the elec-

trodes were coupled externally as in Figure 1, the electro-chemical

reaction was impossible to balance by insertion of an opposing E. M.F.

Further, no difference was noted in the potential of the reactive metal

when coupled with differing noble metals as was the case in Buck and

Leidheiser's work (5) with lead, tin, and iron. They also plotted

potential of the reactive metal vs. the logarithm of the corrosion

rate while immersed in an acid solution containing a noble metal

ion, and showed that the slope (Tafel) corresponded to 2.303 RT/nF

in the case of lead, tin, and iron in selected acids. It is apparent

from Figures 2 and 3 that no such easy correlation can be made, for

measurement of current efficiency may not equal 100 percent. For

instance, at an anode, in addition to the current passing round the

main circuit, there may also be dissolution through local action,

which might include corrosion by current flowing between different

regions of the anode and not registered on the ammeter in the main

circuit. The efficiency may fall below 100 percent if the anode is

particularly passive. In the expected electron change of five, the

Tafel slope at 70° C should be about 13 mv. As can be seen, no

line with such a slope can be drawn, although a positive slope of

67 mv in the case of tantalum corresponding to an electron change

of one, and a negative slope of 33 mv in the case of niobium corres-

ponding to an electron change of two might be imagined from the

sparse scatter of points. The only conclusions that might be drawn

from these data are that the corrosion of niobium in hydrofluoric

acid may be cathodically controlled (from the sign of the slope) and

that of tantalum anodically controlled. Possibly the use of single

crystals in the determinations discussed above might produce more

meaningful data by removing from the system the possibility of

forming "metal-ion" or "differential-aeration cells" between crys-

tals.

It will be noted that of the "platinum" metals ruthenium when

coupled externally with niobium had the largest current flow, as

was also the case of platinum coupled to tantalum. When these

metals were coupled in situ, conversely, the dissolution rates were

not the fastest. When a noble metal, such as ruthenium was added,

in the case of niobium or platinum; in the case of tantalum the noble

metal did indeed quickly reduce and form a precipitate on the surface

of the base metal. However, the reaction then appeared to slow to

a very low rate. Examination of the noble metal film under the hand

glass revealed a pore-free appearing film. Tactile examination

revealed this film to be a slime.

The mechanism of dissolution of niobium and tantalum in the proposed method might be described as follows: When a pure metal corrodes in a non-oxidizing acid, an anodic reaction and a cathodic reaction occurs on the surface of the metal:

$$
\begin{array}{c|c}
1 & M = M^{n+} + n(e) \\[2mm]
n & H^+ + 1(e) = \frac{1}{2}H_2 \\
\hline
\end{array}
$$
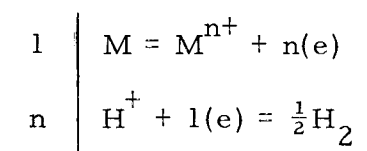
quite likely at contiguous points, or even at the same point at different moments. When tantalum and especially niobium are contacted with hydrofluoric acid these reactions are sometimes difficult to initiate, unless a very strong oxidant such as nitric acid is used. When a more noble metal, such as platinum is added in solution, it will immediately precipitate and the reaction rate increases drastically. The platinum, having a lower hydrogen can be readily eliminated, and freeing the whole surface of the base metal for anodic attack.

Two procedures have been proposed based upon dissolution promoted by the in situ coupling of "platinum" metals with niobium and tantalum for the determination of nitrogen. The latter involves a novel process which is both rapid and precise. The difference in average values between methods which have been generally accepted in the refractory metals industry and the recommended procedures is readily apparent.

In the case of tantalum analysis, the use of hydrogen peroxide presents the problem of having a blank which is low because of an indeterminate amount of nitrogen which is reduced in the presence of the metallic sample, and therefore gives high values in the nitrogen assay of the sample. As hydrogen peroxide always contains some nitrogen either as an impurity or as a preservative, and in part consists of nitrate, hydrogen peroxide is not recommended as being ideal. The data and the vendors assay indicates that the hydrogen peroxide used contained approximately 18 micrograms nitrate expressed as nitrogen per milliliter. While the error induced by this amount of nitrate is not too critical at the level of 0.01 percent, it is obvious that at 0.001 percent nitrogen in high purity tantalum the relative error becomes overwhelming.

In the case of niobium, a sacrifice was made (in the use of hydrogen peroxide) to permit dissolution of the sample within a reasonable period of time. The decreased yield using the standard method could be caused in two possible ways: Kirk's suggestion (15) of a loss of nitrogen in the presence of a bisulfate media and a failure to decompose a portion of the nitrides. After considering these two possibilities, it was proved that the latter was more probable, since subsequent treatment of the sulfate fusion with hydrofluoric acid and "platinum" metals did indeed yield the additional nitrogen. This process, unfortunately, is not feasible as an analytical method

because of the high and erratic blank values apparently caused by the extensive manipulation of the sample. In addition the data using the recommended method less hydrogen peroxide also proves the sulfate fusion to be inadequate.

The use of hydrogen peroxide and the subsequent fuming in sulfuric acid probably account for the poor precision using the recommended procedure for nitrogen in niobium and obviates its use in high purity material. It is felt, however, that at the level of 0.01 percent and above that the improvement in accuracy greatly overshadows the loss in precision. In high purity niobium, the omission of hydrogen peroxide and dissolution in a capped bottle would be recommended, except for the dissolution time of three to four weeks.

After much of this work was complete Jaworowski (13) published his procedure for dissolving niobium and tantalum preparatory to determining nitrogen. Comparison of values by this obtained on a sintered niobium powder sampled by milling show correlation similar to that of the "proposed" method. The same sample was not suitable because of the time lapse since the original work was done with attendant nitrogen pickup of the sample and because Jaworowski's dissolution method is too violetnt for finely divided samples, causing ejection of a portion from solution. Similar correlation has been obtained on tantalum.

In conclusion, two procedures are proposed which are rapid, accurate, and in one case precise. While the procedures are not as rapid as the Jaworowski method, they confirm that method, and remain the method of choice for very finely divided samples.

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APPENDIX

APPENDIX

(1) The Determination of Nitrogen in Columbium by the Method of

Van Santen and Valder (25)

Dissolution:

Weigh accurately 1.0 grams into a clean 500 ml Kjeldahl

flask. Keep covered at all times, except during fusion. Add

five to ten grams of potassium pyrosulfate. Add 10 ml of con-

centrated sulfuric acid. Fuse to clear (neglect carbon) over a

Fisher burner and allow to cool.

Distillation:

A 250 ml Erlenmeyer flask is prepared by rinsing with

deionized water, then adding 10 ml of 0.15 percent boric acid

solution and two drops of mixed brom cresol green-methyl red

indicator. The delivery tube of the condenser is rinsed with

deionized water and the receiver flask placed under the con-

denser so the delivery tube extends below the liquid surface.

The Kjeldahl flask is connected to the distillation apparatus and

40 to 50 ml of 50 percent sodium hydroxide solution added

through the funnel. Distillation is started by introducing steam

to the unit, and 30 ml of distillate collected.

Titration:

The distillate is titrated to a pink end-point with 0.00357 $\underline{N}$

hydrochloric acid, and compared to the end-point of a blank.

(2) The Determination of Nitrogen in Tantalum by the Method of

Mallett (18)

Dissolution:

Transfer a 0.5 gram sample to a 40 ml platinum crucible.

Add 5 ml of 1:1 sulfuric acid along with 2 ml of hydrofluoric acid

and 1 ml of 30 percent hydrogen peroxide. Cover with a platinum

lid and heat on a hot plate until the major part of hydrofluoric

acid is driven off. Repeat if a residue remains unreacted, mak-

ing certain that all of the hydrogen peroxide has decomposed

before proceeding to the distillation.

Distillation:

Transfer the diluted sample solution to a Parnas-Wagner

still and add 25 ml of 38 percent sodium hydroxide solution.

Distill and collect the condensate in a 50 ml Erlenmeyer flask

containing four drops of mixed brom cresol green-methyl indi-

cator and 10 ml of 0.15 percent boric acid solution.

Titration:

Titrate the collected ammonia with standard acid, and make

a blank determination using the same amounts of all reagents as

in the sample determination.

(3) Niobium Dissolution by the method of Jaworowski (13)

Dissolution:

Weigh accurately 0.3 gram into a Teflon beaker. Add 6 ml of 24 percent hydrofluoric acid and one gram of potassium iodate. Cover with a polypropylene clock glass.

Distillation:

Dilute with about 25 ml of water and quantitatively transfer to a steam distillation unit. Add 25 ml of 30 percent sodium hydroxide and steam distill. Determine the ammonia in the distillate by any convenient method.