MASTER

IMPROVED SAMPLE BONDING AND EMISSION
WITH TANTALUM SURFACE IONIZATION FILAMENTS

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A B S T R A C T

Techniques for conditioning of tantalum filaments for improved bonding and emission with a tantalum metal powder-tantalum pentoxide mixture are described. A porous tantalum metal layer is deposited which restricts sample to the filament. Metal-oxide ion emission is enhanced with additional tantalum pentoxide to the porous layer.

Reduction of fractionation through action of liquid tantalum pentoxide is discussed in particular for Sr^+ emission.

Use of conditioned filaments for rapid uranium concentration analysis with a single-filament mass spectrometer is emphasized.

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SUMMARY

Conditioning of tantalum filaments with a tantalum metal powder-tantalum pentoxide mixture improves sample bonding, increases filament efficiency, and stabilizes emission from tantalum surface ionization filaments. Precision mass analysis is made possible from greatly reduced sample quantities as a result. The tantalum powder particles are joined together and to the filament through deposition of tantalum metal from the oxide under surface ionization conditions. A porous tantalum metal layer is formed through this action, and, for this stage of conditioning, the term "porous tantalum metal filament" is used. Sample flaking and evaporation losses are inhibited, and the filament is strengthened against warping and vibration with this initial process.

The tantalum metal powder-tantalum pentoxide mixture in itself enhances metal-oxide ion emission for certain sample species; therefore, in addition to the process for deposition of porous tantalum metal, an additional layer of mixture to which sample is applied directly, may be used for increased sensitivity, in particular, for UO_2^+ emission. Filaments so conditioned in two stages are designated as "Ta-Ta₂O₅ filaments", and are used mainly at ICPP for rapid, precise uranium analysis by isotope dilution.

Because of the possibility of increased fractionation through repeated condensation of neutral evaporated species, tests for fractionation effect were made. Results show that the ratio U-233/U-238 remains constant during very long UO_2^+ emission periods; also, that fractionation effect is essentially eliminated for the Sr^+ spectrum from SrO . Reduced fractionation effect is believed to result from miscibility of sample species with liquid tantalum pentoxide above 1870° centigrade.

Very little time is required for the conditioning process, and advantages of a single-filament instrument for rapid analyses are maintained. Sensitivity for uranium in highly radioactive solution is increased approximately by a factor of 50. Micro analysis for uranium is accordingly much more reliable at the 10^{-4} g/l level than a fluorometric method is at the 10^{-3} g/l level. Reproducibility for uranium determination in terms of isotope dilution mass measurements is $\pm 0.18\%$ at the 95% level. Precision limits in terms of all variables associated with isotope dilution analysis are $\pm 0.35\%$. The latter figure is comparable to precision for a gravimetric technique used in plant final **product analysis**. The Ta-Ta₂O₅ filament therefore enables use of the isotope dilution technique for uranium material balance in all phases of the plant process.

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INTRODUCTION

Good sample bonding on surface ionization filaments results in emission stability, increased sensitivity, and reduced sample requirements. In connection with reactor fuel processing at the Idaho Chemical Processing Plant (ICPP), small sample size is particularly important because of radioactivity. The application of uranium isotope dilution analysis to the plant process is described.¹

Single-filament mass spectrometers with vibrating-reed electrometers were selected for routine analysis at ICPP.² Twenty or more determinations may be required per instrument in an 8-hour shift. Accordingly, multiple-filament instruments are not used for routine production work because of much longer pump down periods. Very small sample quantities suffice with this type of instrument, but the time per analysis is somewhat prohibitive for plant production purposes. The investigation is therefore primarily concerned with a single-filament source and vibrating-reed type detector.

Some techniques which improve bonding or emission from surface ionization filaments include the use of sauerisen cement,³ addition of magnesium powder to borax for sodium borate emission,⁴ and oxidation of the filament surface prior to addition of sample. The latter technique has been found somewhat effective by the writer for UO_2^+ emission from tantalum filaments; however, the filament is weakened and may burn out easily.

Experiments at ICPP laboratories resulted in sample bonding techniques based on a tantalum metal powder-tantalum pentoxide mixture applied to the filament. When preheated under source conditions of temperature and pressure, a deposit of tantalum metal from the oxide joins the metal particles together and to the filament to deposit a porous tantalum metal layer which firmly binds sample to the filament.

Fractionation studies were carried out in connection with these conditioning processes since evaporated species must diffuse through a highly porous metal layer. Repeated condensations could possibly cause or increase fractionation. However, the effect was not observed in the UO_2^+ spectrum. Because of serious fractionation effect observed

by others for strontium isotope analysis,⁵ experiments were carried out to determine effects of the conditioned filament for this element. It was found that fractionation effect is essentially eliminated for the Sr^+ spectrum from SrO . Theoretical views in this respect are given.

FILAMENT CONDITIONING

The ease with which tantalum oxidizes in air at moderate temperature suggests that many sample species would oxidize tantalum filaments at surface ionization temperatures. A reaction between tantalum metal and oxygen is reversible with pressure at high temperature; also above 1870° centigrade the pentoxide exists as a liquid.⁶

The reaction in (1) is important in many surface ionization processes and is the basis for pre-conditioning of tantalum filaments for more efficient ionization. Experiments show that tantalum oxide layers from pre-oxidation, application of Ta_2O_5 , or from reaction with uranium oxides during surface ionization are all transformed to tantalum metal under source conditions of temperature and pressure in accordance with (1). Figure I below shows effects of oxidation by uranium oxide on a tantalum filament.

Figure I. Blistering Effect on Tantalum Filaments by Oxidation with Uranium Oxides.

This particular filament was oxidized by uranium oxide during ionization. The blistered effect resulted from a gradual conversion of liquid tantalum pentoxide to tantalum metal and oxygen as the sample was depleted. X-ray analysis showed only the presence of tantalum metal; however, it is important to note that the melting point of tantalum metal is not reached during a typical uranium analysis.

The increased surface area for the filament of Figure I theoretically condenses more neutral evaporated species which would again have probabilities of becoming ionized. Once the blistered surface is formed, some resistance to sample particle loss might be expected. It is believed also, that miscibility of sample species with liquid tantalum pentoxide can be a critical factor in filament efficiency.

Conditioning of tantalum filaments for the effect of Figure I is ideally accomplished by preheating a mixture of tantalum metal powder-tantalum pentoxide under source conditions of temperature and pressure. In practice, approximately one part metal to three parts pentoxide are finely ground together and applied as an aqueous slurry. At pressures of 10^{-6} mm Hg or less and white heat the reaction in (1) goes to completion in a few seconds. The result is a deposit of tantalum metal which joins the metal particles together and to the filament to give a highly porous metal layer as seen at the bottom of Figure II below.

Figure II. Tantalum Powder Particles Joined by Deposition of Tantalum Metal from Tantalum Pentoxide under Source Conditions.

Sample flaking and evaporation losses are undoubtedly curbed from such a filament because the sample is dispersed within the pores of the Ta deposit. Note the smooth surface for the filament at the top of Figure II. Filament warping, vibration, and degassing with temperature elevation cause sample losses from such a surface before ion productive reactions can occur with the filament.

Certain ionizing processes depend on reaction with Ta metal rather than tantalum oxide, and conditioning need not be carried beyond this stage. UO_2^+ emission however, is considerably enhanced in the presence of tantalum pentoxide. In addition to the porous metal deposit therefore, a layer of the metal-oxide mixture (without preheating) may be applied for increased sensitivity of certain oxide ions. Figure III shows a deposit of finely-ground Ta powder and the pentoxide (darkened by grinding) to which uranyl nitrate solution is applied. The mixture is gradually converted to porous Ta metal at UO_2^+ ionizing temperature. A filament after a typical uranium analysis with this mixture is shown at the bottom of Figure III.

Figure III. Finely Ground Tantalum Powder-Tantalum Pentoxide Mixture for Increased Uranium Sensitivity.

Advantage of filament metal vs filament oxide surfaces for certain metal oxide samples may be seen from the following:

For uranium dioxide the sequence $\text{UO}_2 \longrightarrow \text{UO} \longrightarrow \text{U}$ is inhibited with excess Ta_2O_5 , and UO_2^+ is maintained as the major ion species. During ionization the reaction in (1), under source conditions, proceeds to the right, and oxygen is gradually depleted. Relative abundances of uranium ion species therefore gradually increase in the order from UO_2^+ to UO^+ to U^+ .

The Sr^+ spectrum from SrO is very intense from a porous tantalum metal filament. According to (2), oxidation of tantalum metal by SrO could be a necessary step in the Sr^+ ionizing process, and excess Ta_2O_5 would inhibit such a reaction. This is easily verified experimentally. Sr^+ emission from a smooth tantalum metal surface is difficult to obtain because of poor bonding. A porous tantalum metal filament retains the sample at the high temperature necessary for oxidation. Once this reaction starts, Sr^+ emission is very intense, and SrO^+ ions are scarcely detectable.

FRACTIONATION STUDIES

The conditioning techniques for tantalum filaments possibly cause or increase fractionation because of repeated condensation of neutral evaporated species in diffusing through the porous layer. Experiments indicate however, that fractionation effect is practically eliminated for the relatively light Sr^+ spectrum from a $\text{Sr}(\text{NO}_3)_2$ sample. Fractionation effect would be less serious and possibly very difficult to detect ordinarily in the heavier uranium mass region. Data are presented showing constancy in the ratio $\text{U-233}/\text{U-238}$ for UO_2^+ emission from a $\text{Ta-Ta}_2\text{O}_5$ filament during an extended period. These studies are summarized below in Table I.

TABLE I. Ratios for Sr^+ and UO_2^+ Spectrums with Conditioned Tantalum Filaments.

<u>Elapsed Time-Hrs.</u>	<u>Atom Ratios for Natural Strontium With a Porous Tantalum Metal Filament</u>		
	<u>88/84</u>	<u>87/84</u>	<u>88/86</u>
1	145.4	12.39	8.29
3	144.6	12.37	8.27
7	145.8	12.46	8.26
24	146.7	12.48	8.32

	<u>U-233/U-238 Ratios for a Blended Mixt. With a $\text{Ta-Ta}_2\text{O}_5$ Filament</u>	
1		1.032
3		1.033
5		1.033

It is believed that fractionation is reduced considerably for certain sample species due to miscibility with liquid tantalum pentoxide. Melting points for Ta_2O_5 , UO_2 , SrO , and Sr are 1870° , 2176° , 2430° , and 800° centigrade respectively. A tendency to dissolve in or form solutions with liquid tantalum pentoxide at respective melting points, theoretically, reduces evaporation, and provides more intimate contact with the filament for ionizing efficiency.

Sr⁺ emission from SrO with a porous tantalum metal filament probably occurs according to the sequence:

Absence of serious fractionation effect could be due to low temperature ionization from an intimate mixture for which evaporation is expected to be reduced. Possibly, at temperatures above 800° centigrade (M.P. for Sr), ionization takes place from a liquid film, and fractionation may be reduced somewhat because of this factor as well.

The extent of a fractionation effect, if serious, could possibly be established from several sets of data as given in Table I above. Significant fractionation introduces bias in isotopic abundance analysis unless ion currents are integrated for the entire life of the sample. Such a practice is time consuming and unnecessary, at least, for the UO_2^+ spectrum. Extent of bias from all sources is indicated in agreement with certified isotopic standards. A comparison of results on NBS uranium isotopic standards is given below in Table II. Data were obtained with Ta-Ta₂O₅ filaments within a few minutes after pump down. Day-to-day reproducibility is reflected in individual values each of which includes complete filament preparation and sample loading.

TABLE II. Analysis of NBS Uranium Isotopic Standards with Ta-Ta₂O₅ Filaments.

		NBS		ICPP Values with		
		Wt.%	Stated Values	Ta-Ta ₂ O ₅ Filaments		
NBS U-930	U-234		1.08	1.080	1.083	1.082
	235		93.27	93.252	93.259	93.260
	236		0.205	0.209	0.212	0.212
	238		5.44	5.459	5.446	5.446
NBS U-350	U-234		0.249	0.250	0.253	0.259
	235		34.89	34.942	34.940	34.977
	236		0.170	0.174	0.177	0.177
	238		64.69	64.635	64.630	64.589

ISOTOPE DILUTION ANALYSIS OF URANIUM WITH Ta-Ta₂O₅ FILAMENTS

The isotope dilution technique for uranium analysis at ICPP is based on a U-233 standard containing small amounts of U-234, U-235, and U-238. The mixture of internal standard and sample is separated from radioactive fission products and other impurities by liquid-liquid extraction techniques. Total uranium is expressed in terms of U-233 abundance in the spike and the spiked sample according to the following relationship:

$$\text{U Conc.} = x \left(\frac{F}{f} - 1 \right) \quad (5)$$

Where: (x) is the ratio of quantity of uranium in the U-233 spike to the sample volume. This ratio establishes the units for U Conc.

(F) and (f) are wt. fractions of U-233 in the spike and spiked sample respectively.

Each variable in (5) is measured independently.

Throughout the micro range (f) increases toward (F), and these values are statistically the same below the detection limit. Precision mass analysis reflects small differences in these quantities, and sensitivity is therefore highly dependent on precision. Sensitivity is also increased as the quantity of internal standard is reduced to that of the sample. For micro uranium analysis the Ta-Ta₂O₅ filament is extremely useful in both these respects, because UO₂⁺ emission is maintained very stable at high intensity from much smaller uranium samples. The lower detection limit is extended by approximately a factor of 50 with the Ta-Ta₂O₅ filament as compared to the plain tantalum filament.

For the macro concentration range (f << F) precision in mass analysis is also a very important factor in reliability. Results with the Ta-Ta₂O₅ filament are comparable to a gravimetric technique used on purified uranyl nitrate solutions.

Relationship of overall precision limits for U Conc. at a specified confidence level is given in terms of limits associated with independent variables as follows:

$$L_U = \left[\left(\frac{\partial U}{\partial x} \right)^2 L_x^2 + \left(\frac{\partial U}{\partial F} \right)^2 L_F^2 + \left(\frac{\partial U}{\partial f} \right)^2 L_f^2 \right]^{1/2} \quad (7)$$

Where: L represents limits at a specified confidence level for experimental variances of x, F, and f.

Relative limits are then obtained from (5) and (7) for experimental values of x, F, and f in accordance with:

$$\text{Rel. } L_U = \left[\left(\frac{L_x}{x} \right)^2 + \left(\frac{L_F}{F} \right)^2 + \left(\frac{F}{f} \right)^2 \left(\frac{L_f}{F-f} \right)^2 \right]^{1/2} \quad (8)$$

L_F is most accurately established from (n) observations over several days. Throughout the extreme micro range $(f) \rightarrow (F)$ and therefore, $L_f \approx L_F$. For a random single sample analysis L_F widens by the factor $(n)^{1/2}$ as an approximation of L_f . Table III below shows the manner in which overall precision limits according to (8) are expected to increase as a function of (f) in (5). For these data $F = 0.99936$, $L_F = 0.00003$, $L_f = 0.00008$ (single obs.), $x = 0.02$ g/l, $L_x = 0.0006$. L_x is a function mainly of reproducibility in remotely pipetting a 500 microliter radioactive sample. A 10 microgram U-233 spike is known to within 0.3%.

TABLE III. Precision Limits for Micro Uranium Determination With Ta-Ta₂O₅ Filaments.

Wt. Fraction of U-233 in Spiked Sample (f)	U Conc g/l	Precision Limits at 95% level for U Conc.
0.95177	10 ⁻³	3%
0.99438	10 ⁻⁴	3.5%
0.99886	10 ⁻⁵	17%
0.99931	10 ⁻⁶	175%

In comparison, a fluorophotometric technique used at ICPP on radioactive solutions for micro uranium analysis has approximately the same limits at the 10⁻³ g/l level as is expressed at 10⁻⁵ g/l in the above table.

In the macro range, 95% limits for U Conc. as a function of (f) in (5) are $\pm 0.18\%$ for the Ta-Ta₂O₅ filament as compared to 1.3% for the plain filament. Data for this comparison were taken over a six months period on a constant ratio mixture. Variance in (x) is therefore not a factor, and the difference is due to the type of filament. Limits for (x) in spiking purified uranyl nitrate solution are 0.3%. Therefore, in terms of (8), overall precision limits for U Conc. are $\pm 0.35\%$ for purified uranyl nitrate solution. In comparison, 95% limits associated with a gravimetric technique are $\pm 0.34\%$.

DISCUSSION

A tantalum metal powder-tantalum pentoxide mixture has been used to form porous metal layers on tungsten and rhenium as well as tantalum filaments. Finely divided rhenium when mixed with tantalum pentoxide has also been used to form porous metal layers on various filament surfaces. Tantalum pentoxide was used as the binding medium for rhenium particles since rhenium compounds may be too volatile or are decomposed before their melting points are reached.

Any porous metal layer of high work function on a suitable filament metal should serve to increase filament efficiency. Some sample species undoubtedly react with filament surfaces as a part of the ionizing process. Investigations with deposition of high work function layers on various filament materials could well lead to many specific techniques for difficultly ionized species.

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