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CHEMISTRY IN THE ELECTROMAGNETIC SEPARATION OF TANTALUM ISOTOPES

Boyd Weaver
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CHEMISTRY IN THE ELECTROMAGNETIC SEPARATION OF TANTALUM ISOTOPES

Boyd Weaver, R. L. Bailey and C. W. Sheridan

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ABSTRACT

The chemistry of tantalum is reviewed as it has been applied to the preparation of suitable charge material for the electromagnetic separation of its natural isotopes and the chemical refinement of Ta^{180}.

CHEMISTRY IN THE ELECTROMAGNETIC SEPARATION OF TANTALUM ISOTOPES

Boyd Weaver, R. L. Bailey, and C. W. Sheridan

INTRODUCTION

The recently discovered rare isotope Ta^{180} has been enriched in the production type mass spectrographs at Oak Ridge National Laboratory. Chemists played a part in this project through preparation of charge material for the separation and chemical refinement of the few grams of enriched material, which has been supplied for research in its nuclear properties.

PREPARATION OF CHARGE MATERIAL

Material

Of all the stable compounds of tantalum which could be readily prepared, $TaCl_5$ appeared most suitable. Normally this compound could be prepared most economically by the reaction of Ta_2O_5 with some chlorinating agent such as chlorine in the presence of hot carbon, a mixture of Cl_2 and S_2Cl_2, PCl_5, or CCl_4. However in the present case there was available an adequate supply of scrap tantalum metal in the form of filaments which had been used in ion sources of the mass separators. Hot tantalum metal reacts readily with chlorine. The only precaution necessary in this case was the absence of tungsten and hafnium, which have isotopes of mass 180. These filaments had been used only in the separation of barium isotopes.

Apparatus

Equipment in which this preparation was made is shown in Figures 1 and 2. A Vycor tube about 3 feet long and 2 inches in diameter was supported in an electrically heated tube furnace. One end was constricted and joined to a 10 mm tube terminating in an 18/9 Pyrex male semi-ball joint. This was connected through a gas-washing bottle containing H_2SO_4, to sources of Cl_2 and N_2. The exit end of the reaction tube was fitted with a one-hole rubber stopper, to which was attached a rubber tube leading to the exhaust hood.

Procedure

About 300 grams of tantalum metal was placed in a quartz combustion boat and introduced into the reaction tube. While the furnace was heating to 300°C, nitrogen was passed slowly through the tube. Chlorine was then admitted, nitrogen was stopped, and the temperature was raised slowly to 625°C. The rate of reaction was controlled by controlling the rate of chlorine flow. At high flow rates the tantalum metal was heated to incandescence. Solid $TaCl_5$ deposited in the cool end of the tube. The tube and contents were allowed to cool in a stream of chlorine followed by nitrogen. About 2500 grams was produced.

Product

The product was a pale yellow crystalline solid, which fumed in moist air. Its low boiling point, 242°C, required special control of heat in the mass separator. Tantalum chlorinated under these conditions is in the pentavalent state. This fact was confirmed by carefully hydrolyzing small weighed samples and titrating the HCl released with 1N NaOH. The precipitated Ta_2O_5 was filtered on paper, washed, ignited, and weighed. Both results checked closely the theoretical values for $TaCl_5$.

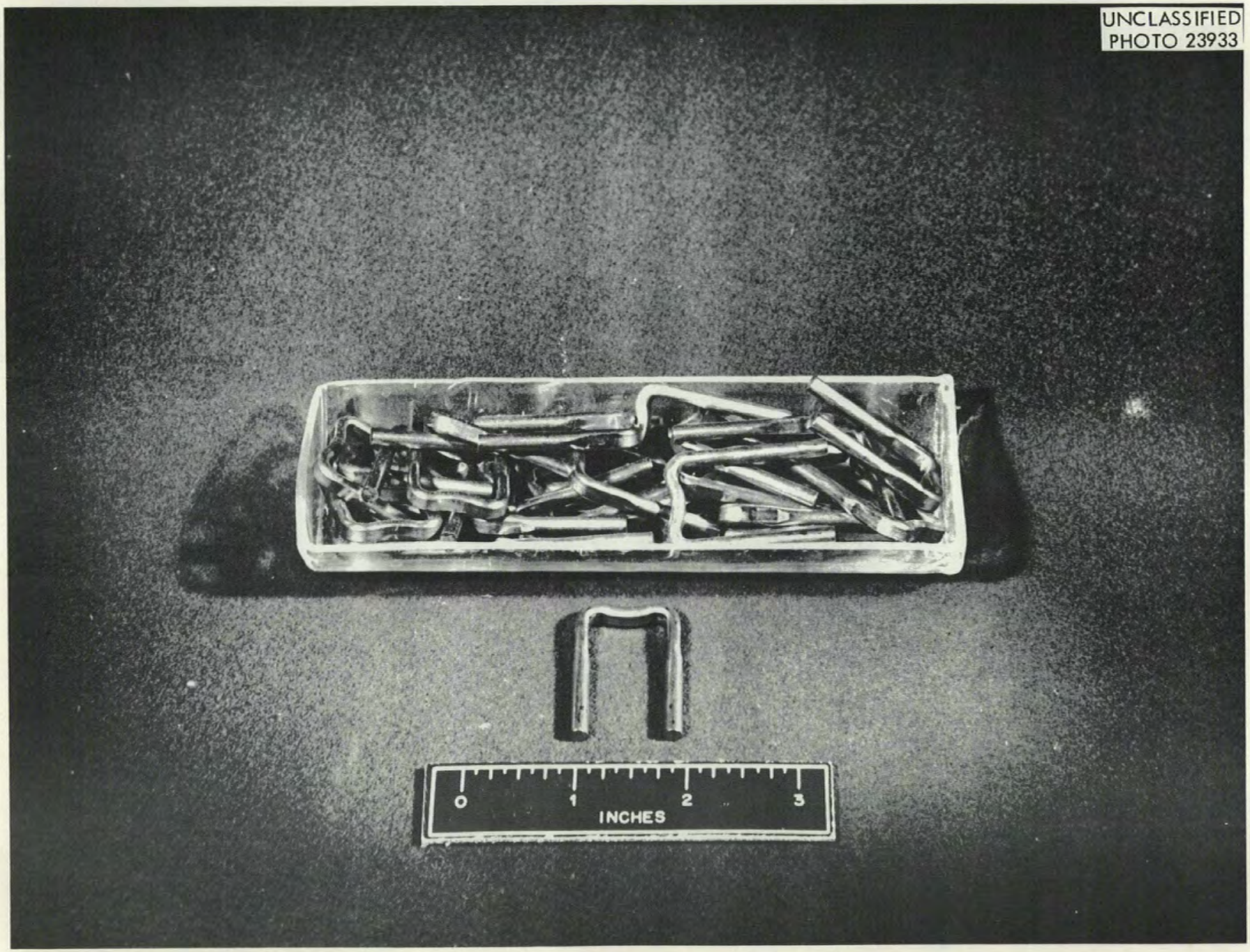

Fig. 1. Tantalum for Charge Material.

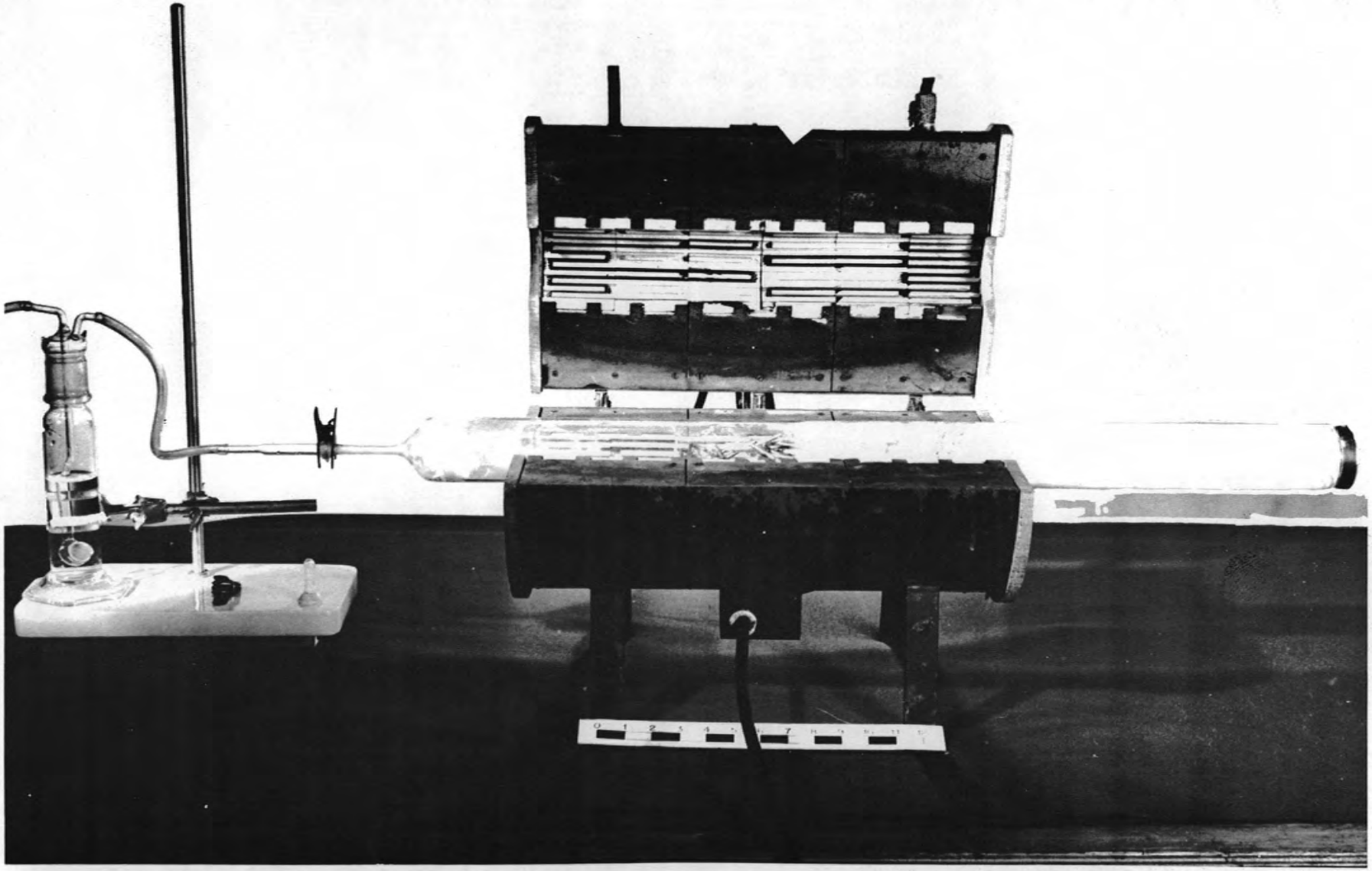

Fig. 2. Tantalum Chlorination Apparatus.

CHEMICAL REFINEMENT

Tantalum isotopes have been collected only in graphite receivers of special designs. Because of the very small mass separation, only about 0.08 inch at the receiver, between Ta^{180} and Ta^{181}, unusual efforts were necessary to decrease contamination of the rare Ta^{180}. Each of the collectors was essentially a graphite box with some kind of partition between the masses. Thus in one case the two isotopes were deposited in part on opposite surfaces of a sheet of graphite tapering in thickness from 1/16 inch to 1/32 inch. An example of a receiver is shown in Figure 3. The Ta was recovered by scraping from the graphite surfaces with a steel tool. Losses of dust were avoided by a vacuum attachment which deposited the scraped material in a sintered glass funnel. Equipment used is shown in Figure 3. The collected material was transferred to a platinum dish and ignited in a stream of oxygen at 600°C.

The impure Ta_2O_5 was dissolved in the dish by heating with a mixture of 1 part 15 N HNO_3 and 4 parts 48% HF. It was usually necessary to make several additions of both acids. The solution was diluted with distilled water and filtered through paper on a plastic funnel into another platinum dish. The tantalum was precipitated with NH_4OH, filtered and redissolved with dilute HF. Three precipitations by NH_4OH were found necessary to remove all traces of copper. The final hydroxide precipitate was dissolved in dilute HF, and an equal volume of 70% $HClO_4$ was added. The solution was boiled to strong fumes of $HClO_4$ and cooled. Tantalum is held in solution only in the presence of HF and precipitates quantitatively from $HClO_4$ as Ta_2O_5. This insolubility was first determined with normal Ta_2O_5.

The precipitate settled so well that most of the acid could be decanted with no loss. The precipitate was washed several times by decantation, first with concentrated HNO_3 and then with dilute acid. The solid was found to peptize in dilute HNO_3 when $HClO_4$ was present. Final acid washings were made on a filter paper. Solids were ignited at 600°C.

On the basis of mass analyses, combinations were made to give three lots with different degrees of enrichment. In one case an attempt was made to decrease the unexpected molybdenum content observed by spectrographic analysis. MoO_3 would be expected to be removed by its solubility in NH_4OH, but it was apparently held in a combined form by the Ta_2O_5. While the oxide had been ignited at only moderate temperatures to prevent difficulties in reprocessing, solution of the batch containing 0.5% MoO_3 required numerous additions of mixed acids while being kept on a hot plate for a period of 3 weeks. The treatment with NH_4OH was repeated. The oxide was then ignited at 1050°C in an attempt to volatilize the MoO_3. Appearance and analysis showed that the treatment was not entirely successful. This material had a yellow color, while the others were white. It is uncertain whether removal of MoO_3 could have been achieved at still higher temperatures. The separation of molybdenum from tantalum appears to be an interesting analytical problem.

DETERMINATION OF PURITY

The chemical purity of refined isotopes is determined by a semiquantitative spectrographic analysis of small samples. The weakest part of the analysis is probably in the sampling. The usual analytical sampling techniques, including grinding, mixing, and dividing, cannot be applied because of the certainty of losses of valuable material and the probability of contamination. Only

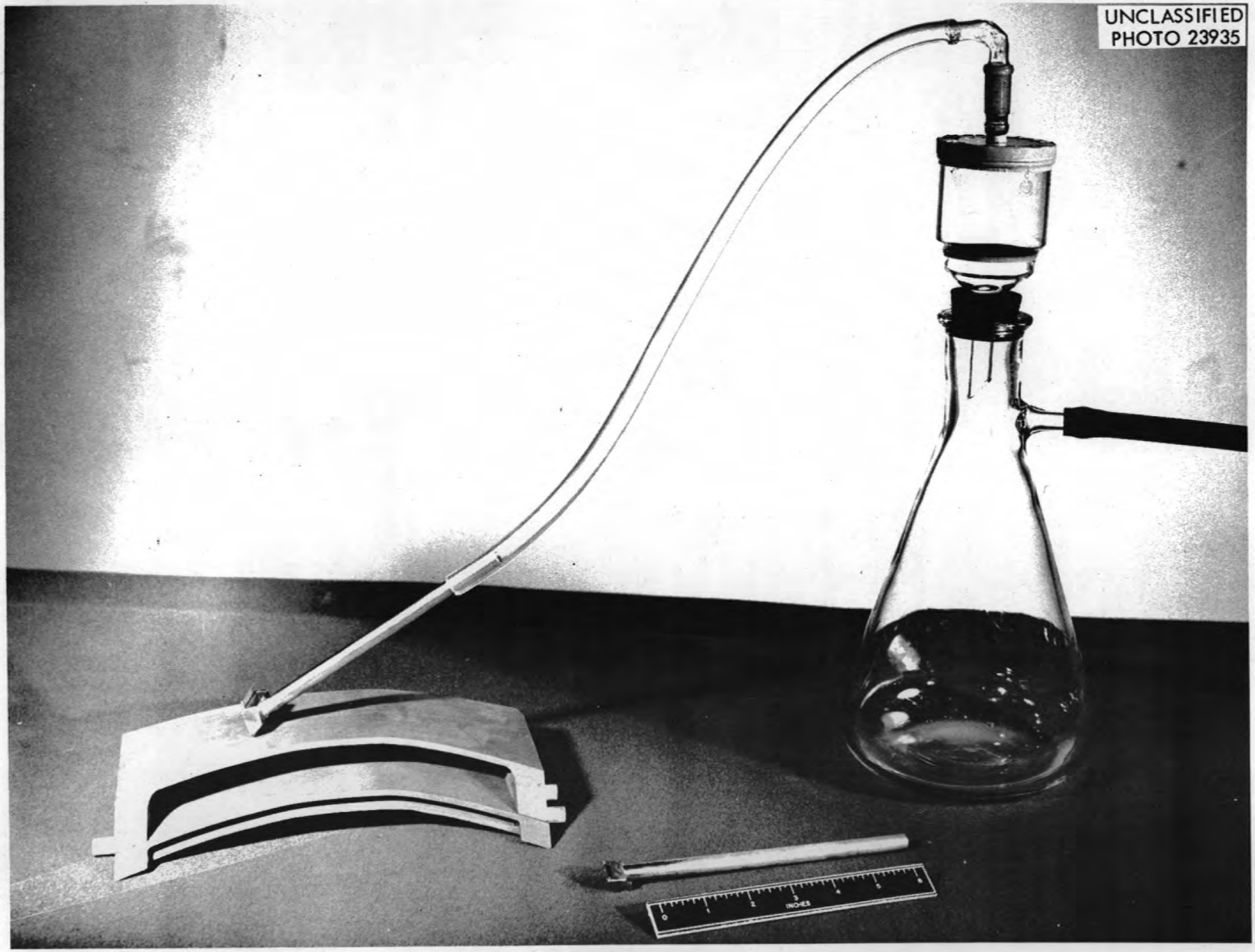

Fig. 3. Apparatus for Recovery of Ta^{180}.

one milligram of material thought to be fairly representative of the whole lot is taken as a sample. The sample is diluted 10 times with graphite as a matrix matrial and burned in an arc. Spectrographic lines are compared with those from standards prepared step-wise. The elements for which search is made are those considered most likely to be present. A separate analysis is required for the alkali metals. The elements sought in analyses of tantalum isotopes and the lower limit of determination, but not of detection, are listed in Table 1. Analyses are on a metal to metal basis.

Table 1. Spectrographic Limits

Element	Limit (%)	Element	Limit (%)
Al	0.05	Mo	0.02
Ba	0.05	Na	0.01
Be	0.001	Nb	0.2
Ca	0.5	Ni	0.05
Co	0.1	Pb	0.1
Cr	0.05	Si	0.05
Cu	0.01	Sn	0.05
Fe	0.05	Ti	0.02
K	0.04	V	0.02
Li	0.01	W	1
Mg	0.01	Zn	0.2
Mn	0.01	Zr	0.1

The quantities of enriched $Ta^{180}{}_2O_5$ placed in the inventory and final spectrographic analyses of these lots are given in Table 2.

Table 2. Ta^{180} Production Data

Lot No.	Weight of Ta_2O_5(g)	Impurities Found (%) Fe	Mg	Mo	Ti
GY 864(a)	2.218		0.02	0.3	0.02
GY 864(c)	0.770	0.02	0.05		
GY 864(d)	1.395		0.02	0.3	0.1

ACKNOWLEDGEMENT

The chemical analysis of $TaCl_5$ was made by W. C. Davis. Spectrographic analyses were by the Spectrochemical Laboratory of this Division under the leadership of J. A. Norris.