LA-2270
CHEMISTRY - GENERAL
(TID-4500, 14th Ed.)

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

REPORT WRITTEN: September 1958

REPORT DISTRIBUTED: February 25, 1959

**THE GRAVIMETRIC DETERMINATION OF TUNGSTEN
IN URANIUM-TUNGSTEN ALLOYS**

by

Robert L. Carpenter
Ross D. Gardner
William H. Ashley
Arthur L. Henicksman

This report expresses the opinions of the author or
authors and does not necessarily reflect the opinions
or views of the Los Alamos Scientific Laboratory.

Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

Tungsten in uranium-tungsten alloys is determined by precipitating the tungsten from a cold sulfuric acid solution using α -benzoinoxime and cinchonine as the precipitating agents. The precipitate is ignited at 800° C and weighed as WO_3 . Results of 94 determinations on known samples containing 20 to 40 milligrams of tungsten in the presence of 1 to 8 grams of uranium showed an average recovery of 100.1 percent with a standard deviation of 0.7 percent.

CONTENTS

	<u>Page</u>
Abstract	3
Introduction	7
Experimental Work	8
Dissolving the Sample	8
Choice of Reagent	9
Apparatus and Reagents	10
Apparatus	10
Reagents	11
Recommended Procedure	11
Reliability of the Method	12
Conclusions	13
References	13

.

.

.

INTRODUCTION

The problem initiating this work was the necessity for determining tungsten with a relative error of less than 1 percent in uranium tungsten alloys containing 0.5 to 5.0 percent tungsten. Because the minimum tungsten concentration was adequate for a gravimetric method, a number of such methods were investigated.

Some of the reagents recommended for the quantitative precipitation of tungsten from solution are: cinchonine;⁽⁶⁾ α -benzoinoxime;^(8,19) rhodamine-B;⁽¹¹⁾ nitron, quinine, brucine, strychnine, and Michler's ketone;⁽¹⁾ codeine;⁽¹⁵⁾ tannin with cinchonine;⁽¹⁰⁾ vanillylidene-benzidine;⁽⁷⁾ o-quinolinol;⁽¹⁴⁾ benzidine hydrochloride;⁽³⁾ 4-4'-diaminostilbene;⁽¹⁸⁾ 8- or 6-toluquinaldine;⁽⁵⁾ β -naphthoquinoline chloride;⁽¹²⁾ calcium chloride;⁽¹⁶⁾ mercurous nitrate;⁽⁹⁾ methylene blue;⁽¹³⁾ and Rivanol.⁽⁴⁾ Duval⁽¹⁾ studied many of the above reagents and came to the conclusion that "a satisfactory practical method for determining tungsten has still to be discovered." However, each of the above reagents was recommended by a worker who considered his method

satisfactory for his particular problem. It was not our aim to find a new reagent for tungsten, but to find something among the reagents already proposed that could be adapted satisfactorily to our problem.

EXPERIMENTAL WORK

Dissolving the Sample

Previous work with uranium-tungsten alloy samples, using a cinchonine procedure similar to that recommended by Hillebrand and Lundell,⁽⁶⁾ had shown that when the sample was dissolved in hydrochloric acid and hydrogen peroxide, most of the tungsten remained undissolved as a heavy black powder. When this was assumed to be pure tungsten and left in the solution to which the cinchonine reagent was added, good results were usually obtained. However, there was always the possibility that something other than tungsten would remain undissolved, so complete dissolution was considered necessary. A mixture of nitric and hydrofluoric acids was effective in dissolving the sample but, because fluorides interfere with the precipitation of tungsten, this had to be followed by a fuming with sulfuric acid. Feigl⁽²⁾ suggested that tungsten samples might be dissolved by a fusion with potassium nitrite. This would also serve as a separation medium because tungsten would be converted to soluble potassium tungstate while most other metals would be converted to insoluble oxides. Two disadvantages were found in this technique. First, the reaction was so violent that it was difficult to avoid some loss of sample, and second, with samples containing only

small percentages of tungsten, too much insoluble matter was formed for good fusions to take place.

The most satisfactory way found for dissolving the sample was to add hydrochloric acid and hydrogen peroxide, which effectively dissolved most of the sample. The insoluble residue was then fused with sodium carbonate.

Choice of Reagent

Digestion with hydrochloric acid and cinchonine⁽⁶⁾ usually gave low results when used with known solutions made up to simulate solutions of uranium-tungsten alloys. This may have been partly due to mechanical losses in the many manipulations involved. The tungstic oxide formed in the digestion process adhered tenaciously to the beaker and the procedure was very time-consuming. The use of tannin with cinchonine as recommended by Lambie⁽¹⁰⁾ sometimes gave good results, but not with sufficient regularity. Benzidine hydrochloride⁽²⁾ and vanillylidene-benzidine⁽⁷⁾ were both tried without success.

Welcher⁽¹⁷⁾ and Knowles⁽⁸⁾ suggested the use of α -benzoinoxime for precipitating tungsten as well as molybdenum. Analysis of known solutions of tungsten using this procedure gave results supporting a statement in Hillebrand and Lundell⁽⁶⁾ that α -benzoinoxime does not always precipitate tungsten quantitatively except in the presence of molybdenum.

Attempts were made to utilize this fact by adding known amounts of

10 minutes filter with vacuum through Whatman No. 41H paper and wash thoroughly with cold, previously prepared wash solution. Burn off the paper in a tared platinum crucible and ignite the residue at 800° C. Weigh as WO_3 , which contains 79.30 percent tungsten.

RELIABILITY OF THE METHOD

Standard solutions of uranium and tungsten were prepared from the pure metals. The uranium was dissolved in hydrochloric acid and hydrogen peroxide. The tungsten was dissolved in nitric and hydrofluoric acids, evaporated to dryness with sulfuric acid, fused with sodium carbonate, and the fused mass dissolved in water. From these standards, aliquots were taken to simulate solutions of uranium-tungsten alloys of different tungsten concentrations and different sample size. The tungsten content of these aliquots was determined by the above procedure with the results shown in Table I.

Table I
RESULTS OF TUNGSTEN ANALYSES OF KNOWN SOLUTIONS

<u>No. of determi- nations</u>	<u>Tungsten added, mg.</u>	<u>Uranium present, grams</u>	<u>Average tungsten found, %</u>	<u>Standard deviation, %</u>
7	40.36	1	100.2	0.7
12	40.36	2	100.1	0.6
12	20.06	1	99.6	0.6
7	30.27	2	99.5	0.5
12	20.09	2	100.1	0.8
32	30.27	3	100.4	0.8
<u>12</u>	<u>40.36</u>	<u>8</u>	<u>100.2</u>	<u>0.6</u>
94			100.1	0.7

CONCLUSIONS

1. Moderate amounts of tungsten in uranium-tungsten alloys can be determined gravimetrically by the use of a combination of cinchonine and α -benzoinoxime as a precipitating reagent.
2. An average recovery of 100.1 percent with a standard deviation of 0.7 percent was obtained for 94 determinations of known amounts of tungsten varying from 20 to 40 milligrams in the presence of 1 to 8 grams of uranium.
3. The method is relatively rapid and simple. No long digestion times are required, and the precipitate does not adhere to the glassware too tightly to be removed with a rubber policeman.

REFERENCES

- (1) Duval, C., "Inorganic Thermogravimetric Analysis," p. 419, Elsevier Publishing Company, New York, 1953.
- (2) Feigl, F., "Spot Tests," Vol. I, 4th ed., p. 117, Elsevier Publishing Company, New York, 1954.
- (3) Feigl, F., "Spot Tests," Vol. I, 4th ed., p. 375, Elsevier Publishing Company, New York, 1954.
- (4) Golubtsova, R. B., Zhur. Anal. Khim., 8, 105-9 (1953). C. A., 47, 10404 (1953).
- (5) Golubtsova, R. B., and Shemyakin, F. M., Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R., 3, 241-5 (1951). C. A., 47, 2636 (1953).
- (6) Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis," 2nd ed. pp. 686-93, John Wiley and Sons, Inc., New York, 1953.
- (7) Hovorka, V., Collection Czechoslov. Chem. Commun., 10, 518-26 (1938). C. A., 1624 (1939).

- (8) Knowles, H. B., Bur. Standards J. Research, 2, 1-7 (1932).
- (9) Konopik, N., Österr. Chemiker-Z., 52, 196-7 (1951). C. A., 48, 77 (1954).
- (10) Lambie, D. A., Analyst, 64, 481-490 (1939).
- (11) Oats, J. T., Eng. Mining J., 144, (4), 72-3 (1943). C. A., 37, 3694 (1943).
- (12) Platunov, B. A., Vestnik Leningrad.Univ., 7, (12), Ser. Mat., Fiz. i Khim., 137-41 (1952). C. A., 48, 4356 (1954).
- (13) Platunov, B. A., Deitch, A. E., Vestnik Leningrad.Univ., (6), 45-63 (1950). C. A., 47, 12117 (1953).
- (14) Přibil, R., Sedlář, V., Chem. listy, 44, 200-4 (1950). C. A., 45, 5564 (1951).
- (15) Shu-Chuan, L., Kan-Nan, C., Sci. Record (China), 2, 295-302 (1949). C. A., 44, 10583 (1950).
- (16) Sousa, A. de, Anal. Chim. Acta., 2, 309-13 (1953).
- (17) Welcher, F. J., "Organic Analytical Reagents," Vol. III, p. 246, D. Van Nostrand Co., New York, 1947.
- (18) West, T. S., Metallurgia, 47, 97-106 (1953). C. A., 47, 4791 (1953).
- (19) Yagoda, H., Fales, H. A., J. Am. Chem. Soc., 60, 640-643 (1938).