323
4-20-65

MASTER

LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS of the NEW MEXICO
University of California

THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM
IN MIXTURES OF URANIUM AND MOLYBDENUM

PATENT CLEARANCE OBTAINED. RELEASE TO
THE PUBLIC IS APPROVED. PROCEDURES
ARE ON FILE IN THE RECEIVING SECTION.

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

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.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

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.

Printed in USA. Charge \$ 2.00. Available from the U. S. Atomic Energy Commission, Technical Information Service Extension, P. O. Box 1001, Oak Ridge, Tennessee. Please direct to the same address inquiries covering the procurement of other classified AEC reports.

LA-3226
UC-4, CHEMISTRY
TID-4500 (37th Ed.)

LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS ██████████ of the ██████████ NEW MEXICO
University of California

Report written: January 1965

Report distributed: March 27, 1965

THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM
IN MIXTURES OF URANIUM AND MOLYBDENUM

by

A. D. Hues
A. L. Henicksman

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ABSTRACT

The spectrophotometric determination of uranium with 3-(2-arsonophenyl-azo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid was modified and applied in the presence of large amounts of molybdenum, which is shown to be without effect. An extensive investigation was made of the interference of numerous foreign ions. The usual masking reagent is ethylenediaminetetraacetic acid. In the present work the use of sodium cyanide as a supplementary complexing agent was found to give significant improvement in the tolerance for cadmium, cobalt, copper, gold, iron, mercury, nickel, ruthenium, and zinc. The relative standard deviation of the procedure is shown to be less than 0.4% for a single determination.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
Abstract	3
Introduction	7
Experimental	9
Equipment and Reagents	9
Exploration of the Method and the Effect of	
Molybdenum	10
The Color Reaction	12
Effect of Diverse Ions	13
Masking Agents	17
Apparatus and Reagents	19
Calibration Curve	20
Sample Preparation	21
Recommended Procedure	21
Reliability	22
Summary	24
References	24

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

INTRODUCTION

The determination of uranium in the presence of several times as much molybdenum became necessary in the course of a metallurgical research project. Large numbers of samples were anticipated, and ratios of molybdenum to uranium as great as five to one were planned. The required accuracy was not stated explicitly, but was naturally expected to be sufficient to characterize the samples. Molybdenum interferes in the common volumetric methods for uranium,⁽⁹⁾ and procedures for its removal⁽⁷⁾ are slow and difficult. The spectrophotometric determination of uranium with thiocyanate⁽³⁾ is rapid, but it is also sensitive to the presence of molybdenum. It was found that, with careful control of acidity, electrolysis with a mercury cathode reduced the molybdenum content to a level tolerable in the thiocyanate method, but with the added steps the procedure was long and quite exacting. A final complication occurred when certain samples which had been heated to more than 2000° C could not be analyzed by this method. The results were reproducible but as much as several percent too high. The cause of the difficulty was never ascertained, but renewed efforts were made to find a more satisfactory method.

Fritz and Richard⁽²⁾ published a quantitative method for the determination of uranium using Arsenazo [3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid]. In their method, the use of EDTA (ethylenediaminetetraacetic acid) made it possible to determine uranium in the presence of many common elements without separation - a very desirable feature. Among the interferences surveyed was molybdenum, which they reported did not interfere at a concentration about 10 times as great as the uranium. Dahlby and Waterbury⁽¹⁾ had also done some work with an essentially similar method, and they had found that there was less than 1 percent bias from the presence of 40 times as much molybdenum.

This paper presents a detailed report of the investigation of the use of Arsenazo in the presence of molybdenum. Extensive work was done to learn the effects of various foreign ions and to develop countermeasures for those interferences that were found. Both Fritz and Dahlby used EDTA to mask interfering ions, and this reagent is a very useful one. However, the amount of free EDTA that may be present without diminishing the uranium-arsenazo color is quite small, and some supplementary masking agent less damaging to the color reaction was sought. Sodium cyanide was found to be very satisfactory. Significant improvement was observed in the permissible amounts of cadmium, cobalt, gold, iron, mercury, nickel, ruthenium, and zinc. Very large amounts of cadmium, cobalt, copper, nickel, and zinc can be satisfactorily masked by the use of large amounts of this cyanide in a slightly modified procedure.

EXPERIMENTAL

Equipment and Reagents

The calibrations of the volumetric flasks for this use were rechecked, and flasks in error by more than 0.1 percent of the nominal capacity were removed. Similarly, recalibrated transfer pipets were used for volume measurements. Volumes of 1 milliliter or less were measured with micropipets calibrated for washout. Addition of the buffer solution with adequate precision was readily accomplished by use of an automatic reservoir pipet (Machlett), but the addition of Arsenazo reagent solution was more troublesome. Because of absorption by the excess reagent it was necessary to measure the amount added to about 0.02 milliliter in order to secure the best reproducibility in the samples. A 5-milliliter Koch reservoir buret has been used satisfactorily, and it is fairly rapid.

Standard solutions of uranium, molybdenum, and other metals were prepared from the metals or salts of analytical reagent quality. For the most part the procedural details were taken from the work of Fritz or Dahlby, whichever seemed more convenient. The innovation of using phenolphthalein for the approximate adjustment of pH before adding the buffer solution has proven very satisfactory in routine use.

Exploration of the Method and the Effect of Molybdenum

Under the conditions of the recommended procedure it was found that the plot of absorbance versus micrograms of uranium was linear up to at least 200 micrograms of uranium. A solution containing 25 micrograms in a volume of 25 milliliters has an absorbance of about 0.100, and the use of smaller amounts of uranium will involve some sacrifice of precision. When it became necessary to measure smaller absolute amounts of uranium, two adjustments were made in the procedure.⁽⁶⁾ The amount of Arsenazo solution was reduced to 1 milliliter, still very carefully measured, and the absorbance was measured in 5-centimeter cells. It was found that when a correction was made for the difference in the length of the absorption cells, the calibration curve was continuous with that obtained by the regular procedure. The standard deviation was found to be about 1 percent down to 10 micrograms of uranium, rising to about 10 percent at 1 microgram.

Measured quantities of uranium and molybdenum standard solutions were mixed to simulate the most unfavorable ratio that was expected in the samples -- five times as much molybdenum as uranium. These were analyzed by the recommended method, and the results compared with those from solutions containing similar amounts of uranium only. It was found that there was no difference between the two sets of values. This comparison was made several times, and there was never a measurable difference.

As had been noted by Dahlby, the development of the color was somewhat slow in the presence of molybdenum. With uranium alone, color development is nearly instantaneous, but in the presence of large amounts of molybdenum the color continues to increase during the first 30 minutes. A little extra time was given in the recommended procedure. The further changes in absorbance of some typical samples are shown in Table I.

Table I
Variation of Absorbance with Time

Sample No.	<u>1 hr.</u>	<u>3 hr.</u>	<u>6 hr.</u>	<u>22 hr.</u>
12	0.758	0.760	0.761	0.766
15	0.760	0.759	0.761	0.770
11	0.770	0.767	0.772	0.773

After waiting 1 hour the samples may be read at leisure, but they should not be left overnight.

As work progressed it became necessary to analyze samples containing much larger ratios of molybdenum to uranium. Known mixtures were analyzed with ratios of 200:1, 2,000:1, and finally 12,000:1. At the ratios of 200 and 2,000 to 1, there was an increase in absorbance during the second half-hour, but no change after that. In the 12,000:1 mixtures, 2 hours were required to reach the maximum absorbance. The uranium measured in samples containing 200 and 2,000 times as much molybdenum was within 1 percent of that actually present. At a 12,000

to 1 ratio, where only a few micrograms of uranium were being measured, the recovery was 104 percent, in acceptable agreement with previous experience in the same range.⁽⁴⁾

As part of the program to establish the validity of the method, a group of pieces that had been heat treated at various temperatures was analyzed extensively. Sixty-four samples were analyzed for uranium by the recommended procedure and for molybdenum by a gravimetric method using α -benzoin oxime.⁽⁸⁾ The two analytical values were summed for each sample, using the assumption that all molybdenum was present as metal and all uranium as uranium dioxide. The 64 sums had an average value of 100.1 percent with a standard deviation of 0.4 percent. These samples, which had been heated at high temperatures, were of the same type as those that had previously given difficulty with the thiocyanate method. However, when they were also analyzed by the thiocyanate method there was no evidence of the earlier trouble. The average summation with thiocyanate values was also 100.1 percent, but the standard deviation of the sums was 0.8 percent. The greater precision, speed, and simplicity of the Arsenazo procedure make it the obvious choice.

The Color Reaction

The nature of the colored product formed has been investigated by Fritz and Richard⁽²⁾ and Holcomb and Yoe.⁽⁵⁾ It suffices here to say that they found that 1 molecule of the reagent associates with 1 atom of

uranium, and that the molar absorptivity is about 23,000. The maximum absorbance lies in the region 590 to 600 millimicrons. The color reaction is not influenced by normal room temperature variations, and is sufficiently stable for ordinary analytical purposes, though there is some difference of opinion concerning the stability under long storage. The intensity of the color is sensitively dependent upon the pH of the solution.

The full color intensity is developed only with uranium (VI). One drop of bromine water in the acid test aliquot is an effective oxidant, but the measured absorbance should be corrected by subtracting 0.002. In the usual case enough is known of the history of the solution to make this treatment unnecessary.

Effect of Diverse Ions

Arsenazo reacts with a large number of metals and becomes useful only when the selectivity is improved by pH control and the use of masking agents. The triethanolamine-nitric acid buffer described by Fritz has been used very satisfactorily to produce uniform pH values. Fritz and Richard found that EDTA was a versatile masking agent, but the excess must be strictly controlled or it interferes with the development of the uranium color. In the interest of simplicity a weighed quantity of EDTA, as the disodium salt, was incorporated in the buffer solution. In all of the experimental work reported, including the interference studies, this amount of EDTA was present.

The effects of many foreign elements were determined experimentally and the greatest amount of each element that produced an error not greater than 1 percent is shown in column 2 of Table II. Each element was investigated by analyzing a series of 100-microgram uranium samples in which the amount of the element being studied was increased in a regular manner, and each concentration was analyzed at least in triplicate. The level of tolerable interference was set at 1 percent because of the unusual precision of the method itself.

The numerical data shown in Table II must be used with some caution. In most cases the amount of a foreign element that can be tolerated is a direct function of the amount of EDTA or cyanide present, so the individual amounts shown as allowable may not be added. To illustrate, 50 micrograms of either nickel or cobalt can be handled readily, but 50 micrograms of each in the same sample gives a large positive interference.

Hydrochloric, nitric, and perchloric acids are without effect when 50 milligrams of the acid is present in a sample aliquot. Sulfuric acid can be tolerated up to 250 milligrams per sample. Whenever large amounts of acid are present in the sample solution, it is best to use sodium hydroxide for the adjustment of pH, and probably wise to use the pH meter.

The effect of iron is frequently a matter of concern, and its behavior was investigated in some detail. In the regular procedure, iron may be present up to about 10 percent of the amount of uranium. With 10 milli-

Table II
Permissible Amounts of Various Ions

Metal added	Permissible amount (1% error) ^a			
	Recommended procedure	Recommended procedure +10 mg. NaCN	Recommended procedure + 20 mg. tartaric acid	Modified ^c procedure +100 mg. NaCN
Cd	100 γ	3 mg.	---	20 mg.
Cr	100 γ	100 γ	50 γ	---
Co	50 γ	500 γ	50 γ	2 mg.
Cu	25 γ	3 mg.	---	20 mg.
Au	50 γ	100 γ	---	---
Fe	10 γ	50 γ	10 γ	50 γ (500 γ ^d)
Ir	100 γ	100 γ	---	---
Mn	25 γ	25 γ	25 γ	---
Hg	1 mg.	10 mg.	---	---
Mo	10 mg.	---	---	---
Ni	25 γ	3 mg.	---	20 mg.
Nb	2 γ	2 γ	10 γ (100 γ ^b)	---
Pd	100 γ	100 γ	---	---
Pt	100 γ	100 γ	---	---
Rh	100 γ	100 γ	---	---
Ru	25 γ	50 γ	---	---
Ag	5 mg.	5 mg.	---	---
Ta	2 γ	2 γ	10 γ (100 γ ^b)	---
Ti	2 γ	2 γ	100 γ	---
W	---	---	400 γ	---
Zn	50 γ	3 mg.	---	10 mg.
Zr	20 γ	30 γ	20 γ	---

^a All samples contained approximately 100 γ of uranium and 1 mg. of molybdenum.

^b Add 200 mg. of tartaric acid and 10 ml. of Arsenazo reagent. See text, p. 18.

^c See text, p. 18.

^d Add 200 mg. of tartaric acid and 100 mg. of NaCN. See text, p. 16.

grams of sodium cyanide present, this tolerance is increased to 50 percent of the uranium. Tartaric acid alone was ineffectual, but it was observed that a combination of 200 milligrams of tartaric acid with 100 milligrams of sodium cyanide eliminated interference from 500 micrograms of iron in a sample containing 100 micrograms of uranium.

Masking Agents

The use of a standard amount of EDTA in the buffer solution has given very satisfactory service. However, an effort was made to extend the applicability of the procedure. It is the excess of EDTA that must be limited, so if the exact amount of an interfering ion present is known, it is theoretically possible to add the correct amount of EDTA and proceed with the analysis. However, such a method would be of so little practical value that it has not been explored.

Another possibility, and a somewhat more useful one, is to choose some other masking agent that can be used in larger excess. Sodium cyanide is such a reagent, and some work has been done with it. The first point of interest was the amount that could be present without interfering with the development of the uranium-arsenazo color, since that would be the largest amount that could be routinely added to samples. Aliquots containing 100 micrograms of uranium received varying amounts of sodium cyanide, but were otherwise treated by the recommended procedure. With amounts of sodium cyanide greater than 50 milligrams, the phenolphthalein indicator failed and it was necessary to use the pH meter to adjust the acidity to its final value of 7.9. Absorbancies were measured against blanks containing similar amounts of cyanide, and it was found that as much as 100 milligrams of sodium cyanide was without effect. Further increase in the cyanide caused diminishment of the uranium color.

After some exploration with small amounts of cyanide, 10 milligrams was

chosen for intensive investigation. The results are shown in Table II, column 3. With this amount of sodium cyanide added, no change is required in the recommended procedure. Specifically, the phenolphthalein indicator for preliminary adjustment of the pH is satisfactory. Those elements that are masked by cyanide are made allowable in amounts large enough for any ordinary need.

A few elements that form stable cyanides were treated with 100 milligrams of sodium cyanide with the results shown in column 5 of Table II. The alkalinity of the sample solution should be neutralized to a pH of about 8 using the meter, and then the reagents should be added as usual.

Tartaric acid has been shown to be an effective masking agent for titanium, tungsten, niobium, and tantalum. The results obtained with 20 milligrams of tartaric acid present are given in column 4 of Table II. No change in the procedure is necessary with this amount of tartaric acid. In the case of tantalum and niobium, the use of larger amounts of tartaric acid is helpful, allowing the determination of 100 micrograms of uranium in the presence of an equal amount of either. The preferred procedure in the presence of these impurities involves adding 200 milligrams of tartaric acid and 10 milliliters of Arsenazo reagent solution. The pH of the solution is adjusted to 7.9 with sodium hydroxide, using the meter, and then 5 milliliters of the regular buffer solution is added. Full color development is reached in 2 hours at room temperature. This is a change from, and a considerable improve-

ment over, the procedure recommended in a previous report ⁽⁴⁾ in which the solutions were heated to develop the color in a reasonable time. The use of sodium hydroxide appears to be the key, and it is thought that the large amount of ammonium ion introduced in neutralizing strongly acid solutions has a disturbing effect on the buffer system.

APPARATUS AND REAGENTS

Apparatus

Flasks, volumetric, 25-ml., recalibrated. Flasks whose volumes varied from the marking by more than 0.1% were removed.

Pipet, automatic, Machlett, to deliver 5 ml.

Pipets, transfer, recalibrated. Microliter pipets calibrated for washout were used for volumes of 1 ml. or less.

Spectrophotometer, Beckman Model DU, with 1- and 5-cm. cells.

Reagents

Ammonium hydroxide, 10% aqueous, reagent grade.

Arsenazo, 3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, disodium salt. To purify the Eastman Organic Chemicals product, prepare a solution of 2 grams of the salt in approximately 750 ml. of water and filter through a No. 42 paper. Catch the filtrate in 750 ml. of concentrated hydrochloric acid, contained in a suitable beaker and stirred with a magnetic stirrer. The precipitated material should be filtered off on a No. 41-H paper, washed with acetonitrile, scraped off the paper to a watch glass, and dried at 100° C for 1 hour. Dissolve 0.500 gram of the product in 1 liter of water.

Molybdenum standard solution. Dissolve 0.4086 grams of reagent grade ammonium molybdate in water and dilute to 200 ml. This solution contains 1 mg./ml. of molybdenum.

Phenolphthalein solution. Dissolve about 25 mg. of the reagent grade material in 100 ml. of 50% ethanol.

Sodium hydroxide solution, 10% aqueous solution of the reagent grade material.

Triethanolamine buffer. Dissolve 74.5 grams of triethanolamine and 72 mg. of disodium versenate in water. Add 14.0 ml. of concentrated nitric acid and dilute to 1 liter. This solution should be allowed to stand overnight before using.

Uranium standard solution. Prepare a standard solution of uranium by dissolving about 125 mg. (carefully weighed) of ignited Bureau of Standards Sample No. 950 in a little nitric acid and diluting to 1 liter. For routine use it is convenient to seal suitable small portions in glass ampoules for storage. The uranium of Sample No. 950 is the natural isotopic composition, with an average atomic weight of 238.03.

CALIBRATION CURVE

Transfer to 25-ml. volumetric flasks aliquots of the standard uranium solution to contain 20, 50, 100, 150, and 200 micrograms of uranium. Add suitable amounts of the standard molybdenum solution to make the standard aliquots comparable to the anticipated samples. Treat these aliquots according to the directions in Recommended Procedure, and plot the net absorbancies against the known amounts of uranium. The line determined by these points should be straight and should pass through the origin. Calculate the factor to be used in routine work by choosing a point on the line and dividing the number of micrograms of uranium present by the measured absorbance.

Note that if the uranium in the sample analyzed is of an isotopic composition different from the standard solution, the factor derived from the slope of the calibration curve must be suitably adjusted.

The arsenazo reagent solution is stable enough so that a freshly prepared solution can be standardized by analyzing several known aliquots and the resulting value used for 1 or 2 weeks with little sacrifice in accuracy. However, if the uranium standard solution is sealed in ampoules so that it is readily available, the analysis of several aliquots of the standard along with each group of samples assures the accuracy of the sample analysis and takes so little extra time that it readily becomes routine.

SAMPLE PREPARATION

The aliquots taken for analysis will preferably contain from 100 to 200 micrograms of uranium, so the sample size taken should be adjusted suitably. The analyst should make a careful inspection for foreign matter before proceeding with the dissolution. Powder mixtures or cermetts of molybdenum and uranium dioxide yield best to treatment with strong aqua regia. In some cases it may be necessary to take to fumes of sulfuric acid at the end. When the sample solution is diluted to volume it should contain about 5% acid to prevent hydrolysis.

RECOMMENDED PROCEDURE

Analyze all samples in triplicate. For best accuracy analyze standards simultaneously.

Into a 25-ml. volumetric flask, measure an aliquot of sample of such size as to contain 20 to 200 micrograms of uranium. Add 1 drop of phenolphthalein indicator solution, followed by 10% ammonium hydroxide or sodium hydroxide dropwise to a faint pink color. Add 5 ml. of buffer solution. The pink color should disappear. Add 3.00 ml. (carefully measured) of Arsenazo reagent solution, dilute to volume, and mix well.

After 1 hour measure the absorbance at 600 m μ in a 1-cm. cell, using a carefully prepared reagent blank in the reference cell. Make the necessary corrections for differences in the cells. If the sample aliquot contains more than 2 mg. of molybdenum, the absorbance should be measured after 2 hours.

If standards are analyzed simultaneously, divide the micrograms of uranium by the average measured absorbance to calculate the factor. If standards were not analyzed, use the factor calculated in the Calibration Curve section. Be sure that the factor used is correctly adjusted for the isotopic composition of the sample analyzed, and obtain the micrograms of uranium present by multiplying the average absorbance of the sample aliquots by the factor.

RELIABILITY

In the course of the early experimental work to establish the calibration and check the effect of interferences, 66 solutions containing known amounts of uranium were analyzed as standard or control samples. Some of these contained molybdenum and some did not. Two analysts performed this work during a period of about 2 months. When the values were assembled it was found that the standard deviation of a single value was 0.36 relative percent.

The production process started with the preparation of a mixture of powdered molybdenum metal and powdered uranium dioxide. The uniformity of the mixture was investigated by taking about 15 dip samples at random from the mixer batch. In the laboratory each sample was weighed and all of the material was dissolved in order to avoid the uncertainties of further subdivision. Three aliquots of the resulting solution were analyzed by the recommended procedure, and the average value was reported for the sample. To answer the inevitable question of how much of the observed variation was actually present in the samples and how much was contributed by the analysis, all of the data were submitted to the statistical group. By performing an analysis of variance, it was possible to derive estimates of the precision of the analytical method from the three values for a sample. To simplify somewhat, the final result for each sample could then be corrected for the analytical variability, and the remaining variation was attributed to actual

differences in the samples. The analytical variation was generally about 10 to 15 percent of the total observed variation. This whole performance was repeated many times as improved mixing methods were sought. Some representative values of the estimates of the analytical variability, expressed in relative percent as the standard deviation of a single measurement, were 0.41, 0.33, 0.17, 0.21, 0.45, 0.31, and 0.26. The average of these values is 0.31 percent, which is in satisfactory agreement with the previously mentioned estimate of 0.36 percent for a single determination derived from the analysis of known mixtures.

In connection with a sample exchange program originated by the New Brunswick Laboratory, a sample solution containing uranium, molybdenum, and zirconium was analyzed. It was requested that the uranium value be reported on a weight basis, so four weighed portions were taken for analysis. Each was diluted suitably and weighed again. Weight aliquots of the diluted solutions were then taken for analysis, and from this point on the treatment followed the recommended procedure. In this case each sample aliquot had a different absorbance, and it was not possible that the values were smoothed in reading them. From the 24 values obtained, the standard deviation for a single determination was calculated to be 0.38 relative percent. The excellent agreement of this value with our previous experience indicates that equally precise uranium assays would have been obtained by simply following the recommended procedure. The uranium found amounted to 83.97 percent of the weight of the solution, and the average of the values reported by the six participating laboratories was 84.04 percent.

SUMMARY

The determination of uranium with Arsenazo is a fast, precise method, not affected by the presence of large amounts of molybdenum. The use of EDTA as a complexing agent allows the measurement to be made in the presence of many common impurities. The use of sodium cyanide and tartaric acid as supplementary complexing agents has been investigated. The use of this cyanide is shown to make the determination practical in the presence of large amounts of cadmium, cobalt, copper, gold, iron, mercury, nickel, ruthenium, and zinc. Extensive experience with the procedure has established that the relative standard deviation of a single measurement is not more than 0.4 percent.

REFERENCES

- (1) Dahlby, J. W. and Waterbury, G. R., Los Alamos Scientific Laboratory Internal Document, April 1958.
- (2) Fritz, J. S. and Richard, M. J., Anal. Chim. Acta. 20, 164 (1959).
- (3) Henicksman, A. L., Los Alamos Scientific Laboratory Report, LA-1394 (1952).
- (4) Henicksman, A. L. and Hues, A. D., Los Alamos Scientific Laboratory Report, LA-3103 (1964).
- (5) Holcomb, H. P. and Yoe, J. H., Anal. Chem. 32, 612 (1960).
- (6) Hues, A. D. and Henicksman, A. L., Los Alamos Scientific Laboratory Report, LA-2844 (1962).
- (7) Jones, R. J., Ed. "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle," United States Government Printing Office, Washington, D. C., TID 7029, 96 (1963).

- (8) Knowles, H. B., J. Res. Natl. Bur. Std. 9, 1 (1932).
- (9) Rodden, C. J., "Analytical Chemistry of the Manhattan Project," p. 65, McGraw-Hill Book Company, Inc., New York, 1950.