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UNITED STATES ATOMIC ENERGY COMMISSION

ANALYTICAL METHODS AND RESULTS

By
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ANALYTICAL METHODS AND RESULTS

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At the outset of the work described in this report it was decided to carry out the isotopic analysis by means of a measurement of the total alpha particle activity of the samples. The method was in use at Columbia University and at the Bureau of Standards. While it was recognized that the results might be subject to grave errors, the method held promise of sufficient precision for the purpose at hand. Four sources of error must be considered: (1) inconsistencies due to instrumental fluctuations; (2) errors due to the presence of alpha emitters other than the U isotopes; (3) errors due to the ill-defined nature of the preparation used as the alpha particle source; (4) errors due to the physical non-uniformity of the source. Insofar as is possible with the data at hand we will analyze the effect of these errors and present our analytical work in the light of this estimate of accuracy. We may anticipate by remarking that the instrumental difficulties may be eliminated, that radioactive purification is practicable given a sufficiently large sample, but that we have not found a satisfactory method for obtaining a preparation of reproducible composition for the activity determination. We have done no work in an attempt to minimize the effect of the roughness of the sample as prepared for the counter.

The Method of Analysis

The isotopic composition of uranium is, according to Nier⁽¹⁾

	Atom Ratio	Relative Alpha Activity	Half-life
U(238)	139 (+ 1%)	100	4.56×10^9 years
U(235)	1 (+ 1%)	4.6	2.7×10^8
U(234)	0.0032 (+ 10%)	100	7.13×10^4

Since U(234) is genetically related to U(238), any old uranium compound will owe its activity as much to U(234) as to U(238). A process which serves to concentrate the lighter isotopes will, therefore, increase the specific activity of the material. Comparison of the total specific alpha activity of a normal specimen with that of a specimen enriched in the lighter isotopes together with some assumption as to the relative enrichment of U(235) and U(234) enables the estimation of the degree of enrichment of U(235). In effect one measures the enrichment of U(234) and estimates that of U(235). A simple calculation gives the following expression for the ratio of the specific activity of an enriched sample to that of a normal sample:

$$A/A_0 = 1 + 0.01801s + 0.48873s^2$$

(1) A. O. Nier. Phys. Rev. 55, 150 (1939).

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where s and z are such that $1 + s$ and $1 + zs$ are respectively the ratios for a given mass of material of the number of atoms of $U(235)$ and of $U(234)$ in the enriched sample to the corresponding numbers in the normal sample. If one puts $z = 4/3$, that is, if one assumes that the separation process depends directly on mass differences, one finds:

$$s = 1.491(A/A_0 - 1)$$

This expression was used in the calculation of apparent separations. The method of analysis thus requires a determination of a specific activity of a reproducible uranium composition. The first requirement then is that the specimen be free from chemical impurities.

Chemical Purification.

During the early part of the work the purification of the samples was carried out with a view of obtaining uranium preparations free from macroscopic amounts of non-volatile impurities. The steps in the process were as follows:

1. The sample was carried to dryness with HCl to render silica largely insoluble.
2. After taking up in 5N HCl the sample was heated to boiling and gassed with H_2S .
3. The solution was filtered into platinum and heated to expel H_2S . Na_2CO_3 was added to the dilute solution to basic reaction, care being taken to avoid the precipitation of sodium uranate. After standing overnight on the steam bath the solution was filtered.
4. After acidification and heating to remove CO_2 the uranium was precipitated with redistilled ammonia and washed five times by centrifugation with hot $N/4 NH_4Cl$. The precipitate was dissolved in HCl and this process repeated.
5. The ammonium uranate was collected on a sintered porcelain filter and ignited at a red heat in a muffle.
6. The uranous oxide was dissolved in HCl and HNO_3 and evaporated repeatedly to dryness with HCl. The chloride solution was filtered into a weighed crucible and carried to dryness at temperatures but little above 100° .
7. The resulting mass of hydrated uranyl chloride was dissolved in glacial acetic acid (containing dissolved lacquer) to give an approximately 0.05 M solution.

All reagents used were carefully purified. Solvents and acids were distilled in quartz and preserved in vapor vessels.

The discs for alpha particle counting were prepared in the manner described by Spevach and Grosse⁽²⁾.

(2) Jerome Spevach and A. V. Grosse. Columbia University Group. Report. The Preparation of Films of U_3O_8 on Platinum Discs Used in the Determination of Uranium Isotopes by the Counting Method.

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The Ion Chamber and Amplifier.

The alpha particle counter consists of an ion chamber carefully insulated from sound and vibration in conjunction with a six-stage inverse-feed-back linear amplifier. The output of the amplifier actuates a pulse-sharpener and discriminator feeding into a scale-of sixty-four circuit which operates the mechanical counter.

The ion chamber is remarkably free from radioactive contamination: repeatedly the background count over long periods was found to be 1.00 ± 0.05 counts per minute. This background, though scarcely significant as compared to the counting rate of 2000-5000 per minute with a sample in place, was always deducted.

The reliability of the counter may be seen from an inspection of the following table.

Table I

Sample Wt. mg.	Date	Net Count $\times 10^{-6}$	Counts/min./ mg.	Ave.	Fraction of Detns. Within 0.1% of Ave.
5.629	6/9/42	0.728	584.7		
	6/9	0.744	584.9		
	6/9	2.762	584.1		
	6/11	1.103	584.8		
	7/15	1.272	585.6		
	7/30	0.584	585.7	585.0	0.7
3.891	6/19	1.233	607.0		
	6/20	0.957	607.6		
	6/27	0.957	607.3		
	6/28	1.129	607.3		
	8/10	0.993	606.5	607.1	1.0
4.770	6/21	1.784	593.8		
	6/23	1.147	593.5		
	6/24	0.804	593.2		
	6/25	1.947	593.2		
	7/9	1.853	593.1		
	7/11	0.809	593.0		
	7/23	1.139	594.3		
	7/28	0.510	594.0		
	8/1	2.044	593.9		
	8/6	1.150	593.9	593.6	0.9

It is immediately apparent that the agreement is just what one would expect from such a series of measurements of radioactivity. Eighty percent of the determinations lie within 0.1% of the average; the expected distribution for determinations based on 10^6 counts would put 67% of the determinations in this range.

The Balance.

The necessity for accurate weighing of the 3-10 mg films of uranosic oxide demands the most that can be obtained from a micro-balance. We used a new Ainsworth

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Type FVJ balance, which balance is equipped with an optical lever and keyboard weights. The weights were calibrated in terms of a 100 mg weight certified by a Bureau of Standards Class M calibration. The balance was set up in a room maintained at $27 \pm 1^\circ \text{C}$ and at $50 \pm 5\%$ relative humidity. A brass support grounded through the balance case was provided for equilibration of the platinum discs in the balance case. These discs were always weighed against a similar tare. Discs were weighed at least three times, the average of these three or more weighings being taken as the final weight. In the absence of obvious external disturbances no consistent trends were noticed in a series of weighings. The maximum differences between extremes in a group of determinations, carried out by three different operators, picked at random were:

4,2,1,1,1,6,8,4,7,5,7,6,5,2,6,3,5,4,7,3,4,7,2 micrograms.

It is considered that a single determination of weight is accurate to $\pm 2 - 3$ micrograms and hence that our weighings of 3-8 mg films are in most cases accurate to $\pm 0.1\%$.

The Reproducibility of the Oxide Preparation for Counting.

It has been definitely shown that the substance produced on ignition of uranyl salts of volatile acids is not a definite compound, although it does approximate the composition U_3O_8 . One such preparation formed by the ignition of a large quantity of uranyl nitrate showed 84.43, 84.41, 84.41% U. Another preparation showed 84.61, 84.66% U. (The analyses for total U were carried out by reduction in a silver reductor and titration with ceric sulfate standardized against Bureau of Standards arsenious oxide.) The theoretical composition is 84.80% U. Most of our oxide preparations were made by a more or less standardized technique of heating the oxide bearing platinum disc over the flame of a Meker burner. Large variations in composition must have been introduced. Successive heatings for 15 minute periods in a muffle at 650° of a disc carrying about 3 mg of oxide caused increases in weight of 2 - 22 micrograms per heating. The same disc first gained and then lost weight on heating for 15 minute periods at $880 - 900^\circ$. No evidence of stable composition was obtained. Thus any consistency in the counting results must be due to the roughly standardized method of preparing the discs. It is impossible to estimate with any confidence the precision with which the composition of our preparations was reproduced. In view of the possible variation in composition, from UO_2 to UO_3 , assuming an average composition corresponding to U_3O_8 , discrepancies of 3% are not impossible. The counting results do indicate, as will be seen, that the reproducibility is much better than this figure. However, another factor must be taken into account in estimating the reproducibility of the oxide film for counting purposes.

Non-uniformity in thickness of the oxide film must affect the alpha particle activities as determined with our apparatus. The output of the linear amplifier actuates a pulse discriminator. Low voltage pulses, such as might be due to alpha particles which have expended most of their energy in traversing thick layers of solid, will not be recorded. As a matter of fact the pulse discriminator sets a rather sharp lower limit to the energy of alpha particles which are recorded. The effect of the roughness of the film may be estimated from our standard curve (see below): for example, if 10% of the area of the film is 10% thinner than the average, the counting rate is reduced by 0.06%. We have no data on the roughness of our films. We will assume that they were of equal

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roughness and that the maximum uncertainty in the analyses is determined by the composition of the films, which as has been shown may amount to as much as 3%.

The "Standard" Curve.

The following activity data were obtained with a chemically purified U sample from a single source. For purposes of discussion we have arbitrarily selected these data as a standard for comparison.

Table II

Oxide Wt.	Counts/min./mg.	Extrap. Counting Rate	Percent. Diff. Obs. - Calc.
2.970 mg.	615.5	651.8	- 0.5
3.304	614.4	654.8	+ 0.2
3.891	607.3	654.8	+ 0.2
4.770	593.7	652.0	- 0.2
5.629	584.6	653.4	0.0
5.831	583.6	654.8	+ 0.2
6.217	577.3	653.3	0.0
6.410	574.3	652.6	- 0.1
8.154	553.9	653.5	0.0

The best straight line, by the method of least squares, through these points is given by the equation

$$C = 653.5 - 12.22w$$

where C is the counting rate per milligram per minute and w is the weight of the sample in milligrams.

Inspection of the data of Table II leads to an erroneous idea of the precision of the analysis. In spite of the fact that the results are consistent to $\pm 0.3\%$, we must recognize that variations in the technique of preparing the discs for counting could lead to discrepancies of ten times this figure.

It is of some interest to compare these results with the reported value of the total alpha particle activity of uranium⁽³⁾ namely, 25.010 alpha particles per second per milligram of uranium. Our extrapolated activity corresponds to 21.783 alphas per second per milligram of our oxide if we assume that our ion chamber counts one-half of all the alpha particles. Since the diameter of our oxide films is 2-3 centimeters less than the diameter of the collecting plate of the

(3) Kovarik and N. I. Adams. J. Applied Phys. 12, 236-7 (1941)

ion chamber and since edge effects should vanish in the extrapolated activity, such an assumption seems very reasonable. These data give 87.10% U as the average composition of our oxide, a not unreasonable result. In this connection it should be pointed out that the data of Kovarik and Adams depend on the assumption that a certain sample of oxide prepared by Boltwood actually has the composition U_3O_8 . Fortunately some of this oxide is still available. Analyses will be made to determine its composition.

Radioactive Purification of the Samples.

Many members of the three radioactive disintegration series are alpha emitters and are possible contaminants of uranium specimens. For an analysis based on a measurement of total activity such contaminants must be removed with great care. All alpha emitters and all substances of sufficiently long life to be significant which give rise to alpha emitters can be removed from a uranium specimen by precipitation with the following elements:

Ba, Bi, La, Pb, Th, Zr.

Since in not all cases are the radioactive substances to be removed isotopes of these elements, repeated precipitation may be necessary to effect a complete separation. The following two procedures have been used in the radioactive purification.

Procedure I.

Triple precipitations of 10 mg portions each of the carrier elements were carried out as follows:

1. Zr as $ZrO(HPO_4)_2$.
2. Te as Te, by reduction of K_2TeO_3 with Pb metal and HCl.
3. Pb, Ba, Bi, Th, and La as fluorides.

From the dilute sulfuric acid solution obtained after the removal of the excess HF by evaporation in platinum with concentrated sulfuric acid $UO_4 \cdot 2H_2O$ was precipitated by the addition of H_2O_2 , filtered and washed on porcelain and converted to UO_3 by heating at 350° for one hour. The oxide was dissolved in HCl, filtered, and the solution evaporated to give hydrous UO_2Cl_2 .

This method gave a satisfactory quantitative precipitation of Zr, Te, Bi, Th, and La but was not so efficient for Ba and Pb. An effort was made to extend and improve it. The following procedure was finally adopted. It is included here merely for the sake of record; actually no samples have been purified and analyzed by this scheme.

Procedure II.

The following triple precipitations of 10 mg portions of the carrier elements were carried out in the order given:

1. Te as Te, from K_2TeO_3 by Pb.

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2. Pb and Bi as sulfides.

3. Zr as $\text{Zr}(\text{HPO}_4)_2$.

4. Ba as BaSO_4 .

5. La and Th as the fluorides.

Losses of uranium through reduction by Pb and precipitation by phosphoric acid were thus prevented. A much more elaborate purification scheme for the uranium was devised, involving fractional precipitations of some of the uranium under conditions which would remove any platinum contaminant acquired during the sulfuric acid evaporation to remove HF. The procedure is, however, costly in material and will not be discussed here.

Neither of the above procedures is satisfactory for the purification of small samples. With great care and close attention to conditions in the various precipitations satisfactory results with samples as small as 0.1 g might be obtainable. Since in any case the time required for such purifications is so excessive, as routine procedures the methods outlined are of little practical value.

The Analytical Results

The following table summarizes the results of our analyses. In the earlier Brewer-Madorsky experiments the entire cathode portion of the tube, above and below the boundary, was taken for analysis. This was the case with tubes 13, 18, 19, 26, 27. On the remaining tubes only the uranyl chloride solution below the boundary was withdrawn for radioactive analysis.

Table III

Tube No.	Date of Analysis (1942)	Oxide Wt.	Total Counts $\times 10^{-5}$	Counts/min./mg.	100s
13	6/26	5.029 mg	1.099	590.7	0.0%
18	6/22	5.199	1.075	634.4	10.2
	6/22	4.502	2.262	644.2	10.5
26	6/23	3.780	1.499	646.0	8.9
	6/24	4.455	1.026	639.6	9.3
18*	6/27	9.184	1.078	545.6	1.0
	6/27	4.506	0.807	596.9	0.0
26*	6/23	5.608	1.058	578.9	0.0
	6/23	3.952	0.972	600.0	0.0
27	7/9	4.278	1.658	662.9	14.1
	7/10	4.923	3.130	638.9	10.5
39	6/24	5.221	1.935	598.0	2.0
	6/25	4.665	1.327	604.5	1.8
45	7/16	5.286	1.258	597.8	2.1

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Table III (cont.)

Tube No.	Date of Analysis (1942)	Oxide Wt.	Total Counts $\times 10^{-6}$	Counts/min./mg.	100s
48	7/22	4.449	2.790	614.8	3.6
49	7/21	3.621	2.387	616.1	1.5
50	7/22	5.064	1.133	599.9	2.0
51	7/16	6.846	4.139	586.2	3.8
53	7/14	4.910	3.031	605.3	2.7
55	7/15	5.622	3.395	597.9	3.0
57	7/14	6.291	1.337	587.3	2.4
64	8/5	4.403	0.974	601.1	0.5
72-77	8/5	4.763	2.830	599.6	0.9

It is to be remarked that only in those cases in which the entire cathode portion of the tube was withdrawn for analysis were large apparent enrichments found. That these apparent enrichments were due to a concentration of foreign alpha emitters was immediately shown by a repurification, suggested by Professor H. S. Harned, of the samples from tubes 18 and 26. Samples 18* and 26* have been repurified with the addition of an hydrogen sulfide precipitation of bismuth and a sulfate precipitation of barium added as carriers. Radium and polonium must have been largely removed by these procedures. Our further analyses were done as an exploratory measure to find samples worth submitting to a careful radioactive purification. Before any such purifications were attempted the work was discontinued.

It is apparent from these results that no large separations have been found and that no definite conclusions can be drawn as to whether separations smaller than 3% have been effected. This becomes more evident in the light of the data of Table IV, in which is to be found counting results on ordinary material submitted to radioactive purification.

Table IV

Oxide Wt.	Counts/min./mg.	Extrap. Counting Rate
2.782	614.0	648.0
3.379	607.1	648.4
3.977	602.2	650.8
4.531	592.0	647.4
4.839	591.6	650.7

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Table IV (cont.)

Oxide Wt.	Counts/min./mg.	Extrap. Counting Rate
5.498	574.6	641.8 (?)
5.674	580.3	649.6
6.029	577.3	651.0
6.378	568.1	646.0
8.268	538.2	639.2 (?)
8.363	546.2	648.4
9.202	543.9	656.3 (?)

These results are consistently somewhat lower than those from which we have calculated our so-called standard curve. Thus there is a definite possibility that our standard curve was constructed with material containing radioactive contamination. In this connection it should be noted that two discs prepared from material obtained from redistilled UF_6 (supplied by the Columbia University group) gave extrapolated counts of 652.9 and 651.8. Radioactive contamination of this sample must have been small. It is thus unlikely that our standard curve is grossly in error because of foreign alpha emitters.

We believe that our data are sufficient to show that the electrolytic process under the conditions of our experiments has been demonstrated not to give enrichments of $U(235)$ greater than three percent. Whether smaller enrichments have been obtained remains, on the basis of this work, an open question. It is important to note in this connection that only those samples from tubes 18 and 26 have been subjected to radioactive purification. It is probable that such purification would further reduce our apparent separations on samples from other tubes.

We wish to express our indebtedness to the many workers who have contributed to this work. In particular we wish to thank Drs. C. A. Kind and P. J. Bender who carried out most of the radioactive purifications. The ion chamber and amplifier which rendered such good service was constructed under the direction of Professor John R. Dunning, of Columbia University, by Messrs. Harold and Milton Goldberg. We owe them our special thanks.

END

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