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HW-13481

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June 21, 1949

ANALYTICAL RESEARCH GROUP REPORT - REDOX

March and April 1949

H. R. Schmidt

CLASSIFICATION CANCELLED

DATE FEB 27 1957 *jt*

For The Atomic Energy Commission

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FISSION PRODUCTS - Milton Lewis

Zirconium

In view of the fact that mandelic acid* reacts completely with zirconium ion and not with the major components of Redox streams, a new procedure is proposed for determination of this fission product:

1. Precipitate Zr with mandelic acid.
2. Transform the zirconium mandelate to $Zr(OH)_4$ with NaOH, acidify with HCl, and reprecipitate as in step one.
3. Dissolve the precipitate with HF and precipitate $BaZrF_6$.
4. Dissolve the $BaZrF_6$ in H_3BO_3 and HCl.
5. Precipitate the Zr with cupferron.
6. Ignite the cupferrate to ZrO_2 for weighing, mounting and counting.

The above procedure has not been tried as yet in the presence of all the fission products. However, experience with the present $BaZrF_6$ -cupferron procedure indicates that the proposed method will be effective.

The combination of steps 1 and 2 above were shown in the last bi-monthly report to separate Zr quantitatively from all Redox stream constituents. Step 3 will remove the columbium activity which was shown to carry quantitatively on the zirconium mandelate precipitate.

* Kumins, Anal. Chem., 19, 276, (1947).

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Cerium

The procedure for the determination of cerium, as used in the present separations plant, has been tested for interference by Redox stream constituents. Preliminary experiments showed experimental difficulties which can be attributed to one or more of the following causes. These findings are applicable to the analytical work on cerium in the BiPO_4 process.

1. The C. P. cerous nitrate used to make up the carrier solution contained large amounts of impurities, probably other rare earths. This resulted in false figures for recovery of cerium carrier and, consequently, incorrect results for active cerium. Since this effect was noted previously by an independent observer on a different sample of cerous nitrate, it is suggested that cerium carrier be made by dissolving $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and reducing to cerous with H_2O_2 . This salt is more likely to be free of other rare earths. Volumetric analysis of the cerous nitrate carrier gave results 22% lower than gravimetric analysis of the same solution. However, both methods of analysis agreed within 0.4% when the carrier was prepared as suggested above.
2. Self-scattering of the β emission of the sample may increase the counting rate as much as 16% over that for the pure tracer. The counting rate was found to increase with the total weight of precipitate as shown in Figure I. The shaded area indicates the region within which any single determination has a 99% probability of falling. The effect of a fixed amount of solids and varying amounts of radio-cerium is shown in Figure 2. Since almost all the points fall within the 99% limits of the straight line it

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is assumed that the percentage increase in the counting rate is not affected by changes in the amount of activity present.

3. Radiographs of samples of pure tracer evaporated on one inch glass discs showed the activity to be concentrated at the outer edge of the area covered. The disc area covered by the solution was controlled by the location of a sapon ring. The counting rate was found to decrease with increasing area covered. Since the activity was largely at the edge of the disc, the counter window may have cut out some of the radiation. An increase in diameter from 19 mm. to 25 mm. lowered the counting rate 5% at rates of approximately 3400 counts/minute.

The results of the cerium analyses obtained with the pure carrier solution and corrected for self-scattering are shown in Table I. Approximately 6000 counts/minute of radioactive cerium were added to 2 ml. of the indicated solution and these samples were analyzed by the cerium method in CN 2815. The procedure was changed only in that the $Zr(IO_3)_4$ precipitation was done immediately before instead of after the last $Ce(IO_3)_4$ precipitation.

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TABLE I

RESULTS OF CERIUM ANALYSES

<u>Sample</u>	<u>% of Ce activity recovered</u>
1.3 M AlN	90.7, 90.5
1.0 M UNH	123.0, 95.0
0.05 M Fe ⁺⁺⁺	97.7, 97.3
0.2 M Cr ⁺⁺⁺	93.3, 95.6
0.1 M Cr ₂ O ₇ ⁼	95.0, 96.3
0.12 M NH ₂ SO ₃ H	93.7, 95.5
3.9 M NO ₃ ⁻	97.7, 101.4
0.1 M SO ₄ ⁼	97.7, 101.0
Hexone	96.2, 101.8
1.6 M HNO ₃	99.6, 98.4

The data in Table I indicate that the procedure is good to $\pm 5\%$ except in the presence of aluminum.

Since the data of Table I were taken it has been found more satisfactory to mount the samples on 22 mm. microscope cover glasses backed by 1/4-ply showcard cardboard. This gives a perfectly flat mounting and the counting rate is not altered by differences in the height of the sample as was the case with the old mounting on one-inch curved watch glasses backed with aluminum. The data of Figures 1 and 2 were taken with the samples on cover glasses.

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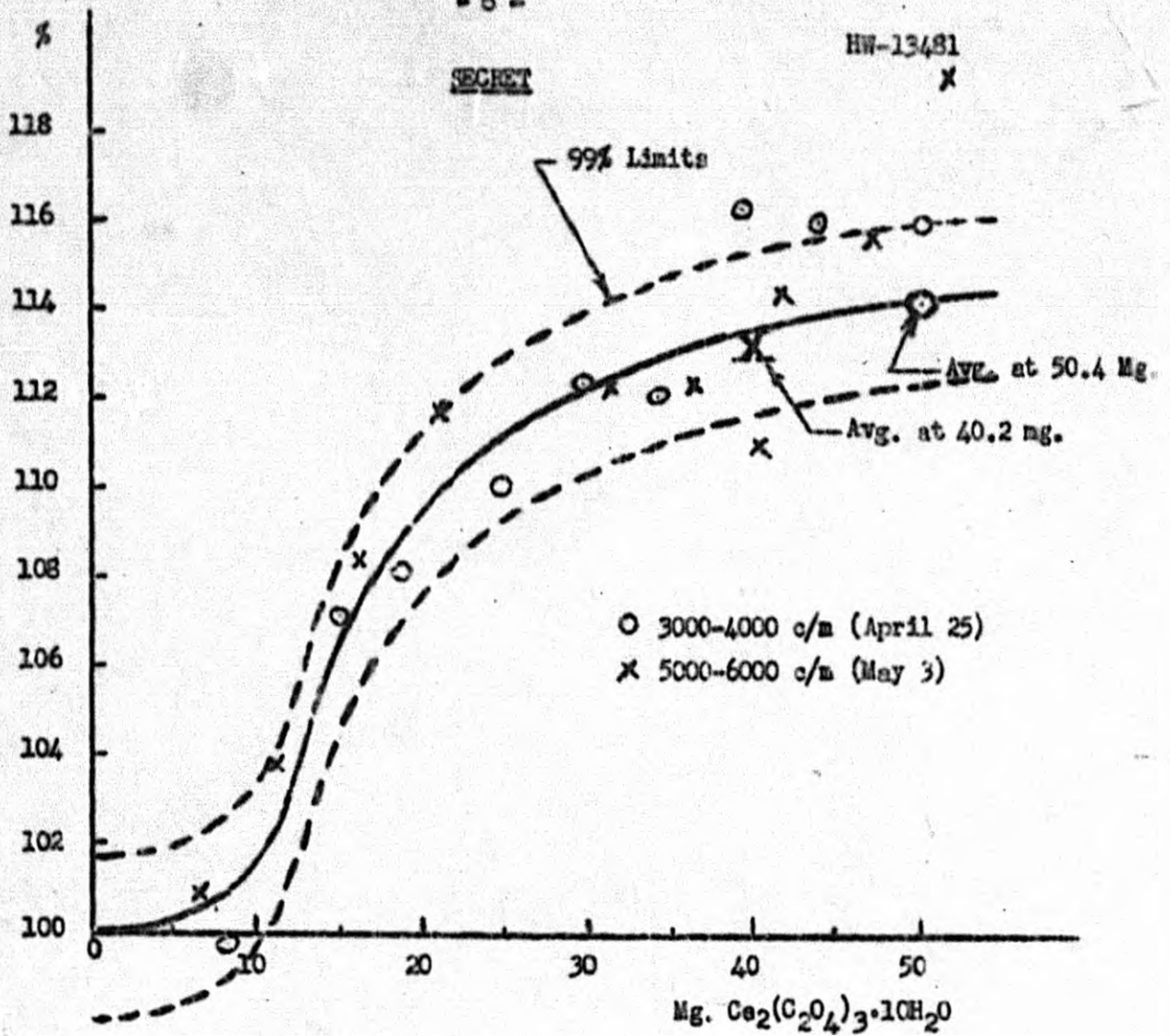


FIGURE I
INCREASE OF COUNTING RATE DUE TO SELF SCATTERING

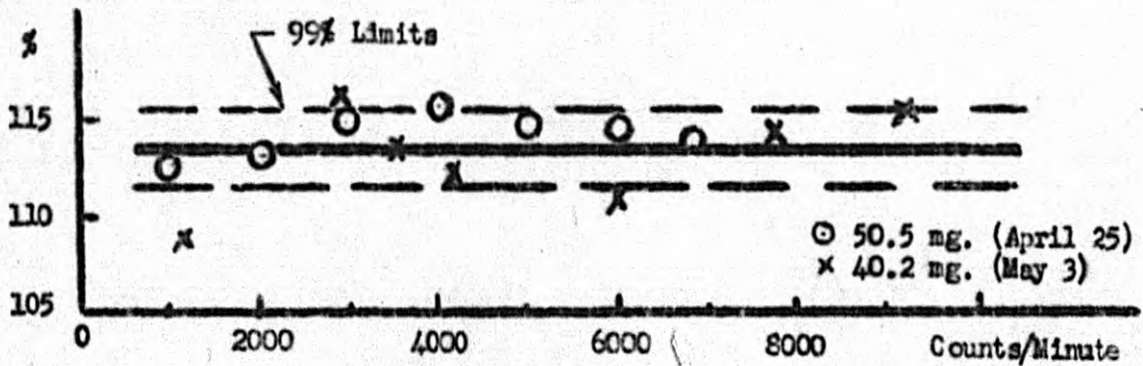


FIGURE II
SELF SCATTERING VS. TOTAL ACTIVITY

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FISSION PRODUCTS - RUTHENIUM - G. J. Alkire

The behavior of the lower valence states of ruthenium in nitric acid solution is not well characterized. In the first place it is difficult to prepare a ruthenium nitrate solution of a particular valence state and identify the state with certainty. Furthermore, the solutions frequently change on standing so that extreme care must be exercised to be sure that the same states exist from one experiment to another. The preparation of ruthenium nitrate solutions followed by polarographic and controlled cathodic reductions of these solutions is being investigated with the hope of elucidating this problem.

A direct treatment of commercial ruthenium chloride, a mixture of Ru III and IV, with nitric acid, produces solutions which contain both ruthenium nitrate and ruthenium nitroso nitrate. Polarograms of these solutions are not clearly defined and cannot be duplicated from one preparation to another. By treating the mixed chloride with chlorine at room temperature a complex chloride is formed with all the ruthenium in the four state (ANL 4265). If this solution is then heated with nitric acid until chloride-free, a reproducible state is obtained as evidenced by identical polarograms and absorption spectra. Solutions prepared in this manner have remained stable for three weeks.

The following polarographic reduction experiments were carried out on ruthenium solutions prepared in this manner. All measurements were made at 25°C and the potentials referred to are those versus a mercury-mercurous sulfate electrode.

Reduction waves of ruthenium nitrate are obtained in 1 M ammonium acetate, 1 M sodium tetraborate, 0.1 M nitric acid, 1 M nitric acid, and 1 M potassium nitrate. Of these

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the nitric acid and potassium nitrate were studied in most detail. In 0.1 M nitric acid, waves are obtained at 0.35 volts and 0.82 volts. There is a slight maximum at 0.5 volts which becomes so prominent in 1 M nitric acid that the reduction steps cannot be measured. This maximum is not removed with ordinary maximum suppressors such as methyl red. One wave only is obtained in potassium nitrate solution at 0.35 volts. However, a mixture of equal parts of 1 M nitric acid and 1 M potassium nitrate yield well defined waves at 0.35 and 0.77 volts. The diffusion current of the first wave increases with concentration up to a certain value then remains constant. The step at 0.77 volts increases irregularly with concentration. The half wave potential of these two waves are independent of the pH from 0.0 to 2.0. A polarogram in this medium is shown in Figure 1. Table I lists half wave potentials and diffusion currents for a series of solutions with various amounts of ruthenium present. Mercury reacts with these solutions very slowly compared to the electrolytic reactions.

Analysis of these two waves shows that each corresponds to a one electron transfer. These data are shown in Table II. This assumes that the reactions are reversible, a point which is now being studied by carrying out macro scale electrolyses at a controlled mercury cathode. Using these reduced solutions, the reversibility or irreversibility of these reactions may be checked by analysis of the anodic wave of the reduced form. Preliminary experiments with solutions prepared at a potential of 0.45 volts corresponding to a value in the diffusion current region of the first wave suggests that this step is irreversible.

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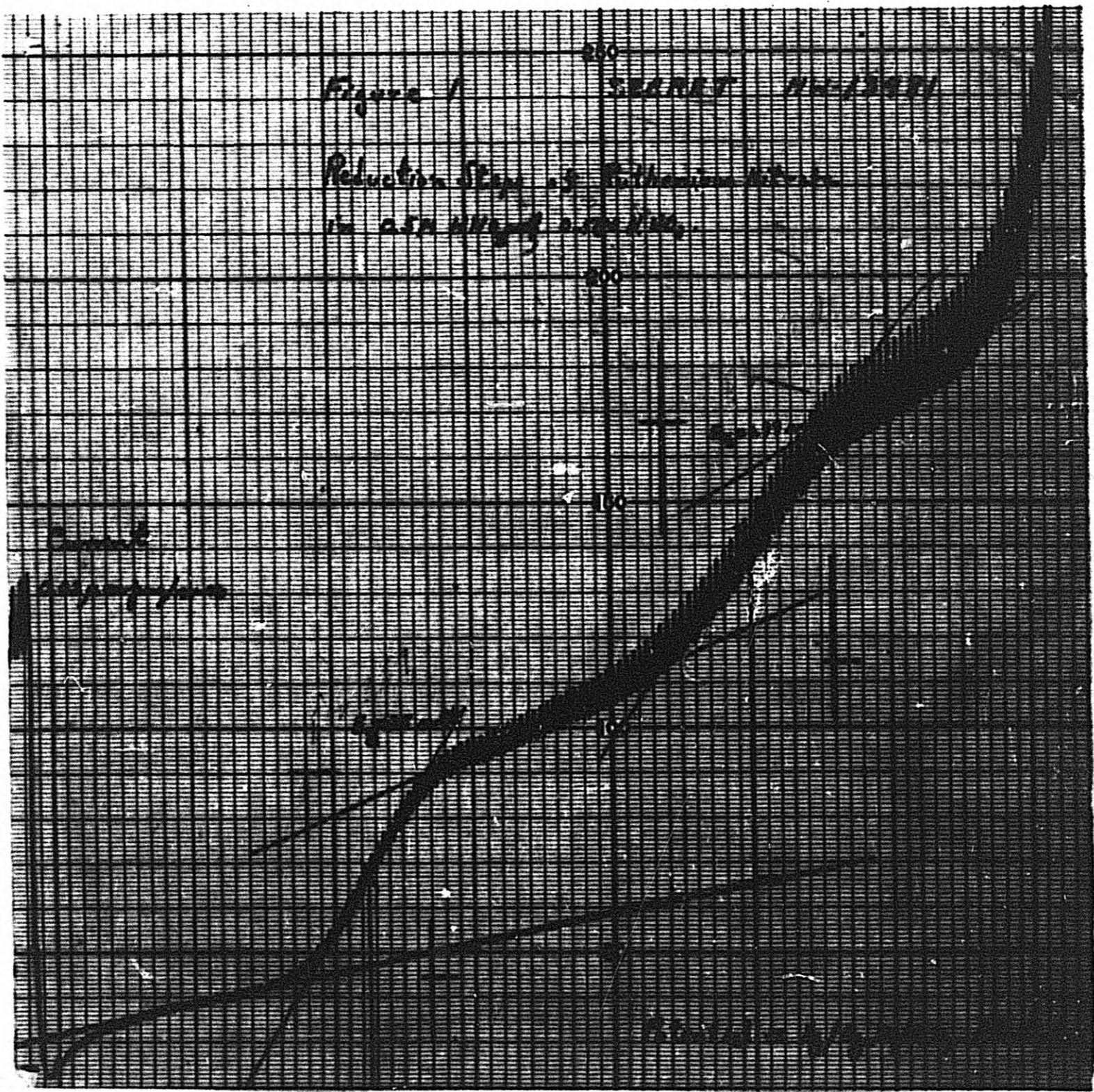


TABLE I

HALF WAVE POTENTIALS AND DIFFUSION CURRENTS FOR RUTHENIUM NITRATE SOLUTION

Lambda Ruthenium Solution in 10 ml Supporting Electrolyte	First Half Wave Potential, Volts	Diffusion Current, Micro Amperes	Second Half Wave Potential, Volts	Diffusion Current, Micro Amperes
100				
300	0.350	0.30	0.770	0.36
500	0.360	0.54	0.769	0.54
700	0.355	0.66	0.770	0.84
1000	0.355	0.72	0.773	0.96
1200	0.360	0.81	0.772	1.32
1400	0.350	0.96	0.770	1.32
1600	0.338	0.84	0.758	1.50
1800	0.350	0.78	0.781	1.14
2000	0.347	0.84	0.775	1.80

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TABLE II

ANALYSIS OF CURRENT VOLTAGE CURVES

Number of Electrons per Mole Equals Slope / .059

Slope at 0.35 Volts	Slope at 0.75 Volts
0.060	0.066
0.057	0.055
0.066	0.055
Average 0.061	Average 0.059

Distillation of RuO_4 into nitric acid and hydrogen peroxide forms what is considered to be Ru (IV) nitrate (ANL 4265). Such a solution gives an absorption maximum at 480 m μ ; the solution prepared by treatment with chlorine and nitric acid gives a very similar absorption curve with a maximum at 480 m μ . Ruthenium (IV) chloride and perchlorate give peaks at 460 and 490 respectively.

From these experiments the following reactions are postulated for ruthenium in nitric acid. Ru (IV) appears to be the most stable state, and is reduced to Ru (III) at 0.35 volts. Ru (III) is reduced to Ru (II) at 0.77 volts which in turn is simultaneously reduced with hydrogen to the metal at more negative potentials.

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Analysis of Uranium Solutions for Nitrite - R. J. Brouns

An investigation was made of the nitrite procedure mentioned in the second and third quarterly reports of the Argonne National Laboratory, Chemical Engineering Division (ANL-4192 and ANL-4228), in order to adapt it to the analysis of uranium solutions. Uranium forms a complex ion with nitrite and, therefore, the usual spectrophotometric method (Method MSN-1a, HW Ion Methods Manual) fails in uranium-containing solutions. The ANL procedure involves the conversion of the nitrite to methyl nitrite, which is distilled into an absorber containing the color-producing reagents. The intensity of the color developed is measured spectrophotometrically in the usual manner. The method was modified to accommodate uranium solutions and it is accurate within 10% for quantities of 2 to 5 micrograms of nitrite.

The distillation apparatus is similar to that used for ruthenium distillation. It consists of a reaction tube and three absorption tubes. The capacities of the tubes range from 30 to 50 ml.; the delivery tube in each absorber ends in a sintered glass bubbler stick. A trap is inserted between the second and third absorbers. The nitrogen inlet to the reaction tube contains a 3-way stopcock, one arm of which terminates in a 1 ml. cup from which phosphoric acid can be admitted to the reaction tube. To each absorber is added, without dilution, 2 ml. of 0.3% amino G solution and 6 ml. of 0.5% *p*-naphthylamine solution. Ten ml. of methyl alcohol and an amount of sample which contains between 2 and 5 micrograms of nitrite is added to the reaction tube. The system is flushed with nitrogen for 5 minutes and then 1 ml. of syrupy phosphoric acid is added to the reaction flask by drawing it in through the inlet stopcock while applying a vacuum to the system. Nitrogen is passed through the system for 15 minutes after which the reagents from the first two absorbers are combined and diluted to 25 ml.

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and the color compared with that of a reagent blank at 530 millimicrons on a Beckman quartz spectrophotometer.

The conditions selected for the development of the nitrite color are not optimum* but they are easily duplicated to give a reproducible color and were chosen for speed and convenience.

Analysis for Volatile Organic Acids in Redox Process Solutions - R. J. Browns

A tentative method of analysis for volatile organic acids in solutions containing uranium, aluminum, dichromate and hexone has been developed. The organic acids, along with the nitric acid, are distilled from a 500 μ sample in a special vacuum still having as a condenser a U-tube immersed in a slurry of dry ice in isopropyl alcohol. Phosphoric acid and ferrous ammonium sulfate are added to the still with the sample. The phosphoric acid liberates the organic acids, which are principally acetic and isobutyric acid. The ferrous ammonium sulfate reduces the dichromate and thereby prevents the oxidation of hexone during the distillation.

The distillate is titrated in an isopropyl alcohol solution with 0.1 N KOH in isopropyl alcohol using a Beckman pH meter and the ordinary glass-calomel electrode system. In 90-95% isopropanol the organic acid ($K_a \sim 10^{-5}$) and nitric acid endpoints are sharp and distinct and the number of ml. between them is a measure of the organic acid present. Any carbonate present will titrate as a weak acid along with the organic acids and therefore all reagents and the solution titrated must be scrupulously protected from atmospheric CO_2 . This is especially true of the alcoholic KOH because a relatively large amount (up to 12 ml.) of it is used to neutralize the nitric acid whereas the organic acids titrated after the nitric acid endpoint require a relatively small amount (as little as 0.1 ml.) of reagent; the percentage error caused by a

* Rider and Mellon, Ind. Eng. Chem., Anal. Ed., 18, 96 (1946)

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small amount of carbon dioxide is thus large. Blanks are run on the reagents daily.

A series of 11 samples of a synthetic IAW containing known amounts of acid gave an average recovery of 100.8% with a standard deviation of 3.82%. The precision at the 99% confidence level was $\pm 9.7\%$.

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UNH DETERMINATION - G. J. Alkire

The application of the manual Hanford Polarograph (HW-13051) to the determination of UNH is being studied. The method depends on the measurement of the diffusion current of the first reduction wave of uranyl ion in hydrochloric acid-hydrazine sulfate solution, as reported in HW-10828.

With the manual apparatus two points, one on the residual current and one on the diffusion current plateau, are measured. The current difference between these two points minus a current difference for a blank is a measure of the diffusion current and hence is proportional to the concentration. The advantages of this instrument are: the initial cost is small, the time for analysis is less than with the ordinary polarographic technique, and it is very simple to operate. It has the disadvantage that irregularities in the current voltage curves will not be observed and false readings may be obtained. It is limited to a smaller concentration range than the regular polarographic technique, but for routine control work it appears well suited.

Table III lists the currents obtained versus the g. UNH per liter in IAW stream samples. Equal parts of IAW and 0.25 M HCl saturated with hydrazine sulfate plus two drops of methyl red were mixed and outgassed at 25° for 15 minutes. The lower value on the residual current was made at 0.03 volts and the upper value at 0.54 volts vs. the S.C.E.

From the data shown in Table III the manual apparatus seems suitable for control work in the concentration ranges shown. These data are being analyzed to determine the precision and accuracy of the procedure.

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CURRENT OBSERVED VS. UNH CONCENTRATION

<u>Grams UNH Per Liter</u>	<u>Number of Determinations</u>	<u>Average Current,* Micro Amperes</u>	<u>Ratio, Conc./Current</u>
0.000	5	0.00	
0.199	6	0.38	0.524
0.298	6	0.66	0.452
0.492	9	1.37	0.359
0.684	6	2.11	0.324
0.965	16	3.40	0.284
1.420	6	5.21	0.273
1.859	12	7.06	0.264
2.281	6	8.98	0.254
2.688	15	10.39	0.259
3.080	10	12.28	0.251
3.460	14	14.41	0.240
3.826	7	16.65	0.231
4.180	7	18.11	0.231
4.854	7	21.04	0.230
5.485	6	24.24	0.226
6.079	6	27.70	0.219

* Corrected for blank average value 0.87 μ amps.

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COULOMETRIC ANALYSIS - W. N. Carson, Jr. and Roy Ko

Titration of 8-hydroxyquinoline

A method, with a precision of $\pm 2\%$ (99% limits) has been developed for the titration of 8-hydroxyquinoline with electrolytically generated bromine. Details of the procedure and equipment used are given in the subject report HW-13000, "The Coulometric Titration of 8-hydroxyquinoline". The sample size used in the investigation was 0.4 to 1.6 mg. 8-hydroxyquinoline.

Titration of Acetic Acid

A method for the titration of acetic acid in the presence of a large amount of HNO_3 by electrolytic generation of base has been developed. Details are given in the subject report HW-13001, "The Coulometric Titration of Acetic Acid". Samples of 50 μg . acetic acid were analyzed with a precision of $\pm 8.5\%$ (99% limits). For 0.12 mg. samples the precision was $\pm 4.5\%$ (99% limits).

GASMETRIC ANALYSES OF NITRITE - W. N. Carson, Jr.

A gas evolution method for determination of nitrite is being investigated. The method involves the reaction of nitrite with sulfamic acid to produce free nitrogen; the nitrogen is collected and measured to effect the determination. The method and apparatus employed are, for the most part, the same as those used in the gasmetric analysis of sulfamic acid as reported in the November-December Monthly Report of this series (HW-12347). The reaction occurring is:



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Analysis of 12 aliquots of an approximately 0.1 M NaNO_2 solution showed a precision of $\pm 0.8\%$ (99% limits). The sample size employed was 200 μl and the volume of gas collected was approximately 0.5 ml. An average value of 4.393 g/L NO_2 was obtained, whereas titration of larger samples with permanganate gave an average value of 4.399 g/L.

An azotometer with 0.1 ml. measuring capacity has been constructed and tested. Analyses of 9 aliquots of an approximately 0.01 M NaNO_2 showed a precision of 7.6% (99% limits). The 200 μl samples were taken and approximately 70 μl of gas were obtained. The average value found was 0.603 g/L; the volumetric value was 0.593 g/L. Most, if not all of the discrepancies could be assigned to error in measuring the blank, due to difficulties in manipulating the azotometer.

ANALYSIS OF GAS FROM HEXONE DECOMPOSITION - W. N. Carson, Jr.

In conjunction with experiments in the Chemical Research Section, a method for the analysis of the gases evolved during decomposition of hexone is being investigated. At present, the gases evolved are swept into a train consisting of an alkaline scrubber, a peroxide scrubber, and the various regulators and control elements used by the investigator. The presence of the following gases was postulated: H_2O , CO , CO_2 , NO , NO_2 , HNO_3 , N_2O , N_2 , HCN , organic acids, and hexone. Analyses for hexone, water and nitrogen were not of interest; preliminary runs showed the absence of CO and HCN . No provision has been made for the determination of N_2O . The alkaline scrub is analyzed for NO_3^- , NO_2^- , and total acid absorbed. Nitrate is determined by the phenol-disulfonic acid method, after destruction of nitrite by sulfamic acid. Nitrite is determined by the Amino-G acid method (reported by R. J. Brouns in this report). Total acid is determined by titrating the excess base to a phenolphthalein endpoint.

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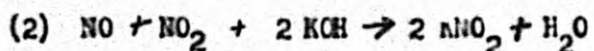
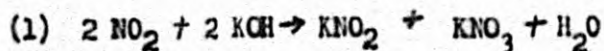
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No successful CO₂ method has been found for analysis of the small sample. By a material balance, the CO₂ and the organic acids comprise about 50% of the total acid gases absorbed, or about 0.1 milliequivalent, of which only one-fifth is available for their determination. The remainder of the sample is used in the other analyses. The peroxide scrubber converts NO into NO₃, which is analyzed by the phenol-disulfonic acid method.

An investigation of the products formed by the absorption of mixtures of NO and NO₂ by alkali is being conducted. Two competing reactions occur:



Present indications are that equation (2) predominates over equation (1) if NO is in excess. Using this as a basis for interpretation, the composition of the gas is determined from the scrubber analyses as follows: NO₃ in the alkaline scrubber is equivalent to the HNO₃; NO₂ is equivalent to twice the NO₂, and the nitrate in the peroxide scrubber plus one-half of the nitrite in the alkaline scrubber is equivalent to the NO.

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PLUTONIUM ANALYSIS - C. B. Barton

After reviewing the work reported previously, it was felt desirable to gain a little more information concerning the precision possible with the TTA extraction procedure and the effect of some of the process components. Accordingly, extractions were carried out in about the same manner as previously reported but with two modifications; the first extraction was with 1 ml. of 0.25 M TTA followed by two extractions with 0.04 M solution. The combined TTA extracts were back-extracted with 6-10 drops of 1 M HF--1 M HNO₃ instead of with 1 ml. portions. In one case the back extractant was changed to 3 M HNO₃ plus 1 drop of 5 M NH₂OH.HCl. This gave poor results due to boiling and bubbling of the liquid by gas evolution on the disk during evaporation. Results are all expressed as per cent of counts of a directly mounted sample of the tracer of the same size. The aqueous phase remaining was analyzed for total remaining Pu by the "hydroxide" method, which will be discussed briefly in connection with the data obtained by its application to tracer samples.

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TABLE I

RECOVERY OF TRACE QUANTITIES OF PU BY TTA METHOD

Medium - 10^{-5} M $Na_2Cr_2O_7$, 0.3 M HNO_3

Sample	Benzene Phase		Aqueous, %	Total Recovery
	Back Extracted, %	Remain- ing, %		
	HNO_3 --HF			
1	93.64	0.12	0.38	94.14
2	92.05	0.21	0.37	92.63
3	3M HNO_3 -- $NH_2OH \cdot HCl$ 59.79	9.15	2.19	71.13
Medium contains process components				
	HNO_3 --HF			
4	95.00	0.44	1.77	97.21
5	84.28	0.98	0.84	86.10
6	85.48	1.00	1.89	88.37
7	89.74	0.07	0.54	90.35
8	85.62	0.33	1.08	87.03
9	74.88 not flamed 90.75 flamed			

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Since TTA is similar to acetyl acetone, which is a recognized reagent for aluminum, it may be surmised that TTA would extract aluminum, especially, at higher TTA concentrations. To determine the possible effects, extractions were performed on solutions containing tracer Pu, 10 μ l. of 10^{-3} M Cr_2O_7 , and 5 μ l. of 1.5 M ANN in 1.5 ml. of 0.33 M HNO_3 .

TABLE II

RECOVERY OF TRACER QUANTITIES OF PU BY TTA

In presence of ANN

Sample	<u>Benzene Phase</u>		Aqueous %	Total Recovery
	Back Extracted, %	Remaining, %		
1	88.15	0.09	0.92	89.13
2	88.99	0.44	0.44	89.77

The total solids extracted were determined by extracting 1.5 ml. of 0.33 M HNO_3 plus 15 μ l. of 1 M ANN with 1 ml. of 0.25 M TTA. This was back-extracted with three 10-drop portions of 1 M HNO_3 -HF. The back-extracts were mounted on a Pt disk and flamed. The disk was weighed, cleaned in HCl and weighed again. The residue was 0.27 mg., which is about 50% of the aluminum present. A similar treatment was applied to the disk bearing sample No. 4 of Table I and the solids were found to be 0.22 mg.

In view of these results, especially the low total recovery, it was decided that no further work on TTA should be undertaken at this time.

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The hydroxide method is currently being used by some of the research control laboratories to determine total Pu. It consists of coprecipitating the Pu with U and La by strong NaOH, leaving the Al in solution. The washed precipitate is dissolved in HNO₃ and treated in the regular manner by the LaF₃ analysis for total Pu. Application of the method to tracer solution gave the following per cent recoveries:

1 - 99.25	5 - 99.49
2 - 99.10	6 - 100.07
3 - 100.83	7 - 99.79
4 - 99.13	8 - 93.68

Thus the method appears to give satisfactory precision.

Since analyses for the separate valence states are desired, the ZFA method for Pu (IV) was examined further to determine its applicability to process streams. Solutions were made up as for the corresponding TTA analyses except that they were 1 μl in HNO₃.

Sample	% Recovered as Pu (IV)	Sample	% Recovered as Pu (IV)
1	93.11	4	96.33
2	95.60	5	94.14
3	92.42	6	96.81

The precision was not adequate, so four determinations were made on pure tracer in 1 μl HNO₃.

Sample	% Recovered as Pu (IV)	Sample	% Recovered as Pu (IV)
1	97.74	3	97.76
2	98.90	4	97.89

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The precision of the above results is quite good and work is underway to prepare stock solutions of Pu (III) and Pu (VI) in addition to the already available Pu (IV). The Pu (III) was prepared by reduction with $\text{NH}_2\text{OH}\cdot\text{HCl}$. Three attempts to oxidize to Pu (VI) with KBrO_3 ($\sim 0.1 \text{ M}$) and heating 1.5 to 2.5 hours in a boiling water bath, were unsuccessful. Lanthanum fluoride analysis indicated 100% carryable Pu. Other oxidizing agents will be tried.

It appears that all the high Pu samples in the Redox process can be satisfactorily handled using some combination of LaF_3 , ZPA, and "hydroxide" methods. Further work is planned to check some of the uncertain streams.

The TTA method appears to need more investigation as to the extractability of many of the process components at the higher TTA concentrations being employed (0.25 to 0.5 M), and the effect of these extracted components on the mounting and counting of the Pu.

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DETERMINATION OF PLUTONIUM II: ICU - E. L. Kinderman

The investigation of wash solutions employed in the lanthanum fluoride method for determination of plutonium was continued. Phosphoric acid, hydrofluoric acid and the usual mixture of nitric and hydrofluoric acids were checked as wash media.

Two-normal phosphoric acid was used to wash a lanthanum fluoride-plutonium fluoride precipitate of 20,000 c/m plutonium. A 500 μ l. portion of the 1000 μ l. wash was removed from contact with the precipitate after suitable time. The evaporation of the phosphoric acid solutions was difficult; much spattering occurred and results were not reproducible. Four samples gave supernate losses ranging from 3000 to 15,000 c/m/ml.

In testing the hydrofluoric acid wash, the solution was made directly over the lanthanum fluoride-plutonium fluoride precipitate by adding 1 ml. of water and 2-4 drops of conc. HF to the centrifuge cone in which the precipitate was contained. No significant difference was noted between use of two and four drops of acid added. The results are shown in Table I.

TABLE I

LOSS OF PLUTONIUM WITH DILUTE HYDROFLUORIC ACID WASH

<u>Pu Present,</u> <u>c/m</u>	<u>Pu Found in Supernate,</u> <u>Average c/m/ml.</u>	<u>99% limits,</u> <u>Average c/m</u>	<u>No. of</u> <u>Determinations</u>
80	0.9	± 1.4	4
800	0.75	± 1.1	3

The nitric acid-hydrofluoric acid wash was made 1 N in each. In the determinations with 20,000 c/m. of plutonium in the lanthanum fluoride-plutonium fluoride precipitate, a steady increase of plutonium in the supernate was observed with time. Results were not reproducible as is shown in Table II.

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TABLE II

VARIATION OF PLUTONIUM LOSS WITH TIME

20,000 c/m Plutonium in Precipitate

1N HF - 1N HNO₃ Wash

<u>Time of Contact, Minutes</u>	<u>Pu in Supernate, *</u> <u>c/m/ml</u>
15	22
35	42
55	86
75	220
87	87
230	62
1260	800

* 10 minute count. Total volume of supernate, 1 ml.

With lesser amounts of plutonium in the precipitate, lesser amounts appear in the supernate. At 80 c/m plutonium in the precipitate a maximum of 1.6 c/m/ml. appeared in the supernate. No real variation of plutonium loss with time was noted. See Table III.

TABLE III

VARIATION OF PLUTONIUM LOSS WITH TIME

80 c/m Plutonium in Precipitate

1N HF - 1N HNO₃ Wash

<u>Time of Contact Minutes</u>	<u>Pu in Supernate *</u> <u>c/m/ml.</u>
85	0 **
105	0.2
115	0 **
125	1.6

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* 10 minute count. Total supernate volume, 1 ml.

** Less than background.

Some attention was given to the loss of plutonium in the precipitation step of the procedure. Several experiments were run during which no control over the initial acidity was maintained (Table IV). Another series of experiments investigated precipitation loss as a function of initial acidity (Table V). This series showed no significant differences in the precipitation losses in the range pH=0 to pH=1. Both series showed small losses of plutonium in the range of expected plutonium content of the ECU. None of the experiments showed variation of plutonium loss with time, for contact times from 20 to 80 minutes. In all cases standard precipitation technique was used. Six drops of conc. HF were added in each case.

TABLE IV

PLUTONIUM LOSS IN PRECIPITATION STEP

LaF₃·PuF₃ Precipitate Formed

No Control of Initial Acidity

<u>Pu Present,</u> <u>c/m.</u>	<u>Pu Loss,</u> <u>Average c/m.</u>	<u>99% limits</u> <u>Average c/m.</u>	<u>No. of</u> <u>Determinations</u>
20,000	138	± 49	4
800	8.0	± 1.4	3
80	1.1	± 2.2	8

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PLUTONIUM LOSS IN PRECIPITATION STEP

LaF₃.PuF₃ Precipitate Formed

Control of Initial Acidity

<u>Pu Present,</u> <u>c/m.</u>	<u>Initial pH</u>	<u>Pu Loss,</u> <u>Average c/m.</u>	<u>99% Limits,</u> <u>Average c/m.</u>	<u>No. of</u> <u>Determinations</u>
570	0.0	6.1	± 5.6	4
490	0.3	3.2	± 4.0	4
480	1.0	0.7	± 3.9	4
60	0.0	1.0	± 2.8	4
120	0.3	9.0	± 5.0	4
70	1.0	1.8	± 3.9	4

In Table V counting precision rather than precision of the experiment is given. The experimental precision is approximately that of the counting technique in the counting range used.

PLUTONIUM IN IAW - E. M. Kinderman

It is supposed that any method developed for the ICU Redox Stream could be adapted to other low plutonium samples. For example, the IAW stream has a low plutonium content and some uranium. A separation of plutonium from uranium should be easier here than in the ICU sample. Before applying the ICU method the aluminum content of the IAW sample must be eliminated or considerably reduced or the method will not be effective. Some work on the separation of aluminum from plutonium has been done by R. E. Burns (HW-9793-Chemical Research Section Report - April, 1948).

In preliminary investigation, the samples used were made by mixing 500 µl of a 1.3% ANN solution with 500 µl. of a Pu (VI) solution counting 500 c/m. NaOH was added to give precipitation of Na₂FuO₇ and solution of NaAlO₂. The supernate was removed

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and the precipitate dissolved. The resulting solution was put through the usual lanthanum fluoride precipitation. The precipitation was followed by three washes of the precipitate. Recoveries of the plutonium were low (<40%). Material balances were ineffective because of the large amounts of aluminum in the first supernate. In a subsequent experiment, 0.25 mg. lanthanum as carrier solution was added to the sample and the identical procedure followed. Recoveries were better (to 80%) but precision was poor.

In further experiments, uranium was added as ICU stock. In four experiments with 2.25 mg. UNH present, recoveries averaged 89.0%. The precision was 1.3%. With 4.5 mg. UNH, recoveries on three experiments averaged 89.6%.

To check the aluminum separation efficiency, two series of experiments were run. In the first, the precipitates of plutonium and uranium (added as 4.5 mg. UNH) from the stock sample were washed three times with dilute NaOH. About 0.8% of the original aluminum was found in the precipitate. In the second experiment, the precipitate was dissolved in acid and reprecipitated with NaOH. About 0.04% of the original aluminum was found in the reprecipitated material. The analysis for aluminum in the presence of uranium is difficult.

Further repetitions of the analysis were made. To the 500 μ l. of 1.3 M ANH and 500 μ l. of plutonium solution (570 c/m), 4.5 mg. UNH was added. Two precipitations with NaOH were made. Samples were allowed 10 minutes for aging and 10 minutes for centrifuging. This was followed by the full ICU procedure given in another section of this report. Results were still far from satisfactory, though precision was good.

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TABLE VI

RECOVERY OF PU FROM SYNTHETIC IAW SOLUTION

570 c/m Pu Present

<u>Experiment</u>	<u>Aliquot</u>	<u>Pu Found, c/m</u>
1	a	407
	b	424
	c	418
	Average	416
2	a	472
	b	473
	c	481
	Average	475

Experiments with larger quantities of plutonium designed to check the merits of lanthanum plus uranium as carrier in the aluminum separation are now in progress.

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DETERMINATION OF PLUTONIUM IN ICU - H. W. Miller

Consideration of Interferences

During the course of this investigation, it was found that the initial pH of the solution was one of the main factors in determining the residual activity of the lanthanum fluoride when precipitated from solutions containing uranium as the only radioactive element. There is some indirect evidence that the nitrate ion contributes to a great extent to this phenomenon. This analysis should not be performed on nitric acid solutions with a pH less than zero, since uranyl fluoride will precipitate out of solution, thus raising the uranium background considerably. On the other hand, if the pH is too high, a diuranate will carry on the lanthanum which will also produce a high uranium background.

The majority of this report is concerned with the effect of the initial pH of the solution on the residual activity of the lanthanum fluoride precipitate. Since the original procedure has been modified to some extent, the procedure used in this investigation will be described below in some detail.

Procedure

After the sample had been adjusted to the desired pH, by the addition of either nitric acid or ammonium hydroxide, 500 μ l. of the sample were placed in a centrifuge cone and the micropipet was rinsed twice into the cone with 1 N HNO_3 . This resulted in 1500 μ l. volume in the cone. Fifty μ l. of 5M $\text{H}_2\text{NOH}\cdot\text{HCl}$ were then added, followed by a 50 μ l. wash of 1 N HNO_3 . After this, 25 μ l. of a solution containing 10.4 mg/ml of La^{+++} were added to the sample and the pipet was rinsed with 25 μ l. of 1 N HNO_3 . Fourteen drops of concentrated HF were added to the sample after which it was stirred and allowed to stand for ten minutes.

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The samples were then centrifuged for five minutes and the supernate withdrawn. About 500 μ l. of a wash solution (1N HNO_3 - 1N HF) was added, stirred, and allowed to set one minute. This was centrifuged for five minutes and the above washing procedure was repeated twice making three washes in all. After the wash supernate was removed, two drops of concentrated HNO_3 were added to the precipitate and then stirred with a platinum wire. Then two drops of 5M $\text{H}_2\text{NCH}_2\text{HCl}$ were added, followed by 500 μ l. of 1N HNO_3 . This was stirred and 14 drops of concentrated HF were added, reforming the LaF_3 precipitate. The sample was allowed to stand 10 minutes and centrifuged for 5 minutes. This reprecipitation process was repeated once more and the sample was then mounted on a platinum disk and counted in the usual manner.

A series of solutions of different pH's were made up and the procedure outlined above was used with the exception that no reprecipitations were performed. The data obtained are listed in Table I.

TABLE I

EFFECT OF pH ON URANIUM CARRIED

No. of Samples	Initial pH	Range	Average c/m	Counting Time
8	0.20	3-23	16	10 minutes
4	0.35	23-43	37	10
8	0.60	9-50	25	10
4	0.85	16-21	19	10

It was found that 14 drops of HF were necessary to insure precipitation of LaF_3 . Samples were run using six drops of HF and there was no apparent variation in the activity of the precipitate. The objection to using six drops is that precipitation does not always occur under these conditions. Since the residual activity of these

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samples was much higher than expected, several reprecipitations were run but the activity never was below the minimum obtained with no reprecipitation.

The above experiments suggested possible contamination with plutonium so another series of solutions was prepared. In this series, reprecipitations lowered the residual activity and made it apparent that at least one reprecipitation should be carried out; this was done in the following experiments.

TABLE II

EFFECT OF pH ON URANIUM CARRIED
One Reprecipitation

No. of Samples	Initial pH	Range	Average c/s	Counting Time
4	0.01	7-9	8	10 minutes
4	0.21	7-9	9	10
4	0.35	4-5	5	10
4	0.61	13-18	15	10
4	0.85	6-11	9	10

A blank was counted before and after each series of four samples. This was then averaged and subtracted from the count obtained.

The same solutions which gave the data above were analyzed again with the exception that two reprecipitations were performed.

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TABLE III

EFFECT OF pH ON URANIUM CARRIED
Two Reprecipitations

No. of Samples	Initial pH	Range	Average c/m	Counting Time
4	0.01	3.2-6.3	4.3	10 Minutes
4	0.21	4.6-4.8	4.7	10
4	0.35	5.5-6.3	5.9	10
4	0.61	3.4-6.0	4.4	10
4	0.85	4.7-6.6	6.1	10

It can be seen, from the data above, that there tends to be a more consistent residual activity after two reprecipitations. Up to the present time, it has been impossible to lower the activity to any significant extent beyond that which is listed above.

As a further attempt to determine the origin of this low activity, a supply of Baker's uranium acetate from a sealed bottle was converted to the nitrate and made up into a synthetic ICU solution. The lot number of this bottle was 11214,* and, therefore, it was assumed to be free from plutonium contamination. The pH of the solution was adjusted to 0.01 and the sample analyzed, using the procedure with two reprecipitations. The results for three experiments in which the pH was 0.1 were:

Range 4.3 to 4.8 c/m

Average 4.6 c/m

If this residual activity were due to Th^{230} there should be about 0.7 c/m/year/sample. This means that if the uranium in the bottle were processed from 5 to 6 years ago, there should be from 3.5 to 4.2 c/m/disk. Since this seemed to agree quite well with * (The November, 1944 date predates extensive project operations).

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the values obtained, it was decided to perform two ether extractions on the sample on the assumption that Th should remain in the aqueous phase and that the uranium alone should go into the ether phase. After the sample was re-extracted into water and made up to the proper concentration, the pH was adjusted to 0.5. Analysis gave the following data:

<u>No. of Samples</u>	<u>pH</u>	<u>Range</u>	<u>Average c/m</u>	<u>Time</u>
4	0.5	2-4	3.3	10

These data would indicate either that the residual activity is not due to Th²³⁰ or that the Th is extracted into ether. The latter alternative does not seem likely.

It was thought that if some impurity were present which carries on the lanthanum fluoride, it should be possible to remove it all by one LaF₃ precipitation and to eliminate any residual activity if the supernate were treated with more lanthanum and hydrofluoric acid. A lanthanum fluoride precipitation was carried out in the usual manner and the supernate was carefully withdrawn and treated as a new sample. This was analyzed in the usual manner with results as in Table IV.

TABLE IV

EFFECT OF SEPARATION FROM A SUPERNATE

<u>No. of Samples</u>	<u>pH</u>	<u>Range</u>	<u>Average c/m</u>	<u>Time</u>
4	0.01	8-25	12	10
4	0.35	12-13	13	10
4*	0.50	11-19	17	10

* An ether extraction was performed on the uranium used to make up this solution.

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These data show a higher residual activity, which was quite contrary to the expected result. The reagents were checked in the same fashion on a sample containing only water and acid. No activity was detected.

It was thought then that this activity might be due to the absorption of uranium due to the reverse strike. This was checked by the addition of HF to the sample before the La^{III} . The procedure was as usual in all other respects.

The data obtained are listed below:

<u>No. of Samples</u>	<u>pH</u>	<u>Range</u>	<u>Average c.p.m.</u>	<u>Time</u>
4	0.5	8-11	30	10

This seems to be fair evidence that the excess activity is due to the reverse strike.

The following points may be brought out in summary:

1. The pH of the solution should be adjusted to between 0 and 1 for a minimum residual activity.
2. At least fourteen drops of HF should be added to insure precipitation of LaF_3 .
3. Two reprecipitations should be performed to obtain a minimum residual activity.
4. The residual activity is in the region of from three to six counts per minute. It has been shown that it is not due to plutonium contamination. If it turns out that Th^{230} can be extracted with ether, the residual activity may be due to this element.
5. It is important that the lanthanum be added to the sample before the hydrofluoric acid due to the reverse strike effect.

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