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ISOLATION AND MEASUREMENT OF URANIUM AT THE MICROGRAM LEVEL

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ABSTRACT

A double cupferron separation of uranium using organic liquid extractions has been adapted to the milligram and microgram levels. Uranium (VI) does not extract as a cupferrate in the first extraction step of this procedure, which serves to remove many potentially interfering elements. Uranium (IV) is obtained in the residual aqueous solution by reduction at a mercury cathode and is simultaneously extracted as the cupferrate into ether, from which it can be reextracted into nitric acid. A relatively simple one-piece glass apparatus is used for all of these operations. The recovery on 0.85 to 4.25 mg. of uranium in an initial sample volume of about 30 ml. was determined colorimetrically as 94.0 ± 1.5%. With 0.03 to 0.13 microgram of radioactive uranium-233 tracer and 20 micrograms of natural uranium as carrier, a recovery of 85.8 ± 1.3% was obtained; the latter figure includes the additional step of electrodeposition of the uranium onto a platinum planchet prior to measurement of the tracer by alpha counting, which step is only 94% complete.

The decontamination possible by using this procedure was checked with 0.07 microgram quantities of uranium-233 (500 c.p.m. alpha) in the presence of mixed fission product activities as high as 130,000 c.p.m. (measured alpha, beta and gamma). A recovery of 85.0% of the uranium-233 tracer was obtained, containing only 0.9% of the fission product alpha activity (which is assumed to be uranium).

ISOLATION AND MEASUREMENT OF URANIUM AT THE MICROGRAM LEVEL

I. INTRODUCTION

With the increasing use of atomic energy for both military and peacetime uses and with the rising cost of extracting uranium from low-grade ores, increasing attention is being given to means of determining and of recovering the small amounts of uranium present in depleted reactor fuels, which are lost by the ordinary means of reprocessing fission products. In addition, investigations dealing with the determination of small amounts of metals have received additional impetus from the increasing awareness of the biological effects of metallic elements in trace amounts. Finally, the disposal of radioactive wastes from atomic installations and the subsequent possibility of the contamination of streams and rivers has created still another reason for developing means for determining and separating out minute amounts of radioactive heavy metals.

Since the beginning of the atomic energy development, a continuing study of the determination of uranium in the concentrational range from the most minute trace levels to practically 100 percent pure metal has been conducted. The present investigation is concerned with the separation and determination of milligram, microgram, and submicrogram quantities of uranium including the recovery and assay of radioactive uranium when it is present in admixture with large amounts of fission products. Since such decontamination may be of importance in removing uranium from fission products, an attempt was made to indicate the manner in which the radioactivity distributes itself in the procedure developed.

In view of the efficiency of liquid-liquid extraction, attention was focused on the separation of uranium by extraction, e.g., of the chelate species which it forms with organic molecules. Measurement at microgram and submicrogram levels of uranium was made through the use of uranium-233 tracer and alpha counting; at higher uranium levels, photometric measurement was utilized. In particular, attention was focused on the development of a procedure which would require simple equipment and only moderate amounts of time, which could be applied to very small amounts of samples and which could be adapted to automatic or semiautomatic manipulation with the minimal introduction of chemical reagents and solvents. Such automatization of analytical processes has obvious advantages and often is an absolute necessity when dealing with such highly radioactive samples as those in which uranium often occurs in admixture with fission products.

II. BASIS FOR THE ANALYTICAL PROCEDURE

Uranyl ion forms a double salt, $UO_2NH_4(Cup)_3$, with cupferron (N-nitrosophenylhydroxylamine) only from neutral solution; this compound is insoluble in organic solvents (1, 5, 6). A second, ether- and chloroform-extractable form appears to exist in acid media (5). Since extraction procedures are particularly attractive for the problem of isolating microgram amounts of uranium from all other elements, the statement (11) that "uranium and antimony are the only elements that will survive a double cupferron separation", becomes of particular interest.

In the conventional double cupferron separation often used in analyzing uranium minerals, an aqueous solution containing the elements in their higher states of oxidation is treated with cupferron and the precipitated cupferrates are removed by filtration or extraction. After destruction of the organic matter in the aqueous phase, the latter is treated with a reducing agent to reduce uranium to U(IV) which is then precipitated with cupferron or extracted with an ether solution of cupferron. Some of the disadvantages of such a procedure for the present investigation would include: (1) the intermediate and tedious step involving destruction of organic matter; (2) contamination resulting from the usual chemical procedures for reduction, e.g., use of zinc columns or liquid amalgams; and (3) the uranium cupferrate ending up in an organic liquid.

Electrochemical reduction of uranyl ion to uranous ion seemed a logical recourse from the second objection. If this could be accomplished in the presence of cupferron, while simultaneously extracting the uranium (IV) cupferrate, as it was formed into an organic layer, there would be no necessity for the intermediate step of destroying organic matter. It seemed reasonable to hope that the third objection could be overcome by extraction of the

uranium cupferrate from ether into aqueous nitric acid and chemical oxidative destruction of residual organic matter. After the appropriate buffering, etc., the resulting solution might be directly usable for the determination of microgram amounts of uranium by electrodeposition and radiochemical counting (14).

The removal of antimony, plus a preliminary removal of some other elements, could almost certainly be achieved by prior extraction of the uranium employing oxine (8-quinolinol or 8-hydroxyquinoline) or substituted oxines. While antimony (III) forms oxinates, antimony (V) does not (2, 10). Uranyl ion may then be reextracted into dilute sulfuric acid, which is a usable medium for the cupferron procedure.

Furman, Mason and Pekola (5) showed that efficient extraction of uranium (IV) cupferrate into ether requires a 5% or more dilute sulfuric acid solution and at least a two-fold excess of cupferron over the 4:1 theoretical requirement; they give distribution coefficients for eight cases with a figure of 88.4 applying for C_{ether}/C_{water} from 1.5 N acid with a 10:1 ratio of cupferron to uranium present. The preparation and general properties of cupferron and its application as an analytical reagent have been summarized in a number of references, e.g., 3, 8, pages 24-25 of 11. As a synthetic organic material, cupferron should not have an objectionably high natural uranium content; it is easily purified by recrystallization from methanol, and is quite stable at room temperature when stored in the absence of light and over ammonium carbonate.

The polarographic behavior of cupferron has been described (9). A polarographic survey (13) of the uranium-cupferron system indicated that the electrochemical reduction of uranium (VI) to uranium (IV) cupferrate and/or uranium (III) cupferrate would be possible in the presence of cupferron at a

potential of about -0.3 volt relative to the saturated calomel electrode. The literature data (5) on the extraction of uranium cupferrates into ether indicated no difficulty in this regard. The reextraction of uranium cupferrates from ether into aqueous nitric acid (with partial decomposition of the cupferron and oxidation of the uranium) seemed feasible.

In the procedure finally developed, the aqueous solution of the sample containing U(VI) is extracted with a solution of cupferron in an organic solvent, such as ether or chloroform, which removes certain metal chelate complexes. The remaining aqueous solution, which contains the uranium is now subjected to controlled cathode potential electrolysis, while the same or a different organic solvent containing cupferron is added to form a separate upper layer. As uranium is reduced by electrolysis to a lower oxidation state, it forms a stable chelate species with the cupferron and is extracted into the organic solvent. The metal ions, originally unextracted, are generally not now extracted with the uranium (IV and/or III); either the electrolysis does not reduce them, or their lower oxidation states do not form species which are extractable. The uranium (IV/III) cupferrate is then reextracted from the ether solution into 7 M nitric acid solution. The nitric acid extract, after decomposition of organic matter with concentrated nitric and perchloric acids, is used for measurement of the uranium.

The uranium isolated as described can be determined by photometric absorption, if as much as a milligram is present. In the case of extremely minute amounts of uranium, these, after suitable chemical treatment, are electroplated onto a small platinum disk whose radioactivity in terms of alpha emission is then measured with a flow counter.

A simple apparative arrangement was devised for the ready conduct of the entire sequence of operations (preextraction, simultaneous reduction

and extraction, and reextraction) on milligram and microgram quantities of uranium.

III. EXPERIMENTAL

A. Apparatus

Details of the reaction cell construction and dimensions are given in Figure 1; the simple electrical circuit used is shown in Figure 2. The electrolysis vessel, C, is protected from mercury ions diffusing from the working reference calomel electrode, A, by a medium glass frit between B and C, and a fine frit backed with an agar plug between B and A. Between runs, the cell C is kept filled with saturated potassium chloride solution.

The first dozen runs of Table I were made using an apparatus similar to that of Figure 1 except that a tubular reference calomel cell of 25-mm. diameter and 95-mm. length was used in place of the 50-ml. Erlenmeyer flask cell; the electrode area of the tubular cell (surface of the mercury and calomel paste) was about one-fourth that of the flask cell. When using the tubular cell, the current flow in presence of milligram quantities of uranium tends to build up a hard crust of calomel over the mercury, resulting in resistances as high as 700 to 1000 ohms. At even relatively low current flow, such resistances result in large iR drops which necessitate excessively high applied potential. When the flask-type calomel cell was used, this was avoided and steady current flow was observed in all runs.

The apparatus for the electrodeposition of uranium onto platinum disks or planchets and for the alpha counting measurement of the resulting uranium plates have been described (12). Beta activity was measured by a chlorine-quenched argon-filled Geiger-Müller counter (1.4 mg/cm^2 window) with a Model 165 scaling unit; a scintillation well-counter with a thallium-activated sodium iodide crystal and a Model 162 scaling unit was used for the measurement of gamma activity from solutions (ca. 5 ml.) contained in a

150-mm. by 13-mm. test tube. Both scalers and both counters are made by Nuclear Instrument and Chemical Corporation. For examination of the gamma-ray spectrum, a gamma-ray scintillation spectrometer (built in the Department of Chemistry, University of Michigan) was used through the courtesy of Dr. W. Wayne Meinke.

B. Uranium Solutions

The radioactive uranium-233 used was obtained as a nitrate solution from the Oak Ridge National Laboratory; isotopic analysis gave 1.0 to 1.5% uranium-232 and 98.5 to 99.0% uranium-233 (alpha 4.82 mev; $t_{\frac{1}{2}} = 1.68 \times 10^5$ y). The original solution (13 μg. of uranium-233) was diluted to 100 ml. which was about 0.01 N in nitric acid; 10 ml. of this solution was diluted to 100 ml. (0.01 N in nitric acid); aliquots of the latter solution containing 1.3×10^{-8} g. uranium per ml. were taken for the experimental work. The activity per microgram of uranium-233 was determined, as subsequently described, to be 7700 ± 88 counts/min. (background subtracted).

A uranyl sulfate solution (0.85 mg. uranium per ml.) which was 0.18 M in sulfuric acid was prepared by dissolving 18.45 grams of the uranyl sulfate trihydrate in 12 liters of 1% sulfuric acid solution.

C. Fission Products

The gross fission products used in testing the procedures were obtained from the Oak Ridge National Laboratory as U. S. Atomic Energy Commission Sample FP-P-1 (2.1 ml., 10mc.), which is a mixture of fission products present as nitrates in 5.4 M nitric acid solution and prepared by separation from heavy metals which have been exposed for from 40 to 60 days in a reactor and cooled only a short time. The total solids were approximately 39.5 mg/ml (iron, ca. 2.0 mg/ml).

A sample (ca. 0.25 mc.), prepared by evaporating an aliquot of the fission products solution on a platinum planchet, was used for examining the gamma-ray spectrum. Three peaks were observed, due probably to cesium-137 (0.661 mev), cerium-141 (0.146 mev), and thulium-170 (0.076 mev). The standards run for calibration were cesium-137 (0.663 mev), chromium-51 (0.33 mev), and thulium-170 (0.085 mev).

The original fission products solution of 2.1 ml was first diluted to 50 ml, 25 ml of which was then diluted to 100 ml (0.1 N in sulfuric acid and 0.05 N in nitric acid). From the latter 1 ml was diluted to 250 ml (0.1 N in sulfuric acid); finally, 5 ml of the latter solution was diluted to 50 ml (0.1 N in sulfuric acid), which solution was used in the experimental work runs; 1 ml of this solution gave 9207 ± 97 alpha counts/min, 1707 ± 61 beta counts/min and 1890 ± 44 gamma counts/min.

D. Reagents

All chemicals used were of C. P. or reagent grade unless otherwise specified. The ethereal cupferron solution used (200 to 300 mg cupferron per 50 ml) was actually a hydrogen cupferrate solution; the ether and cupferron were contacted in a mixing cylinder with 5 to 10 ml of 10 to 20% sulfuric acid and shaken until dissolution was complete.

IV. PROCEDURES

A. Reductive Extraction

At the commencement of a run, bridge B is flushed through stopcock 2 by filling the bridge with fresh potassium chloride solution from the funnel through 1. C is drained and rinsed; 1 is left open for a time to flush the frit. With 3 closed, 4 to 5 ml of triple distilled mercury are placed in C. About 30 ml of uranyl sulfate solution (0.85 to 4.25 mg of uranium) which is 0.5 to 1.5% in sulfuric acid, is added and a potential of -0.35 volt *versus* the reference saturated calomel electrode is applied to the mercury. About 15 to 20 ml of the ether cupferron solution are poured on and the stirring is started. The interfaces normally intersect the expanded disc sections on the glass stirrer. The stirring rate is adjusted at just over the minimal rate that will give an efficient current flow (usually about 0.2 ma flows without stirring, whereas currents of 1.2 to 2.6 ma were obtained during the runs employing stirring).

Stopcock 1 is opened for about 30 sec at approximately 5-min intervals throughout the run to minimize any loss of uranium into the bridge. At 15- or 20-minute intervals, the stirring is interrupted, the ether extract is bled through stopcock 4 into cell D, and 15 to 20 ml of fresh ether-cupferron solution is added. Runs of 40 to 55 minutes total duration appear to be adequate. Three increments of ether-cupferron solution were usually used, followed by a 5 to 10 ml pure ether rinse at the conclusion of the run.

Current readings on the milliammeter vary with time. In some runs the current dropped to a low level soon after the requisite number of coulombs had passed for about a three-electron reduction of the uranium present. In other cases, the current did not drop off, but discontinuance of the run beyond any point where twice the theoretical current had passed gave satisfactory

uranium recovery. In the latter cases, a gray ether-insoluble but alcohol-soluble precipitate (apparently, a mercury cupferrate) was usually evident in the aqueous phase. The current efficiency for the desired process appeared to be good in most runs.

The combined ether extracts may be reextracted in cell D by inserting a clean stirrer and portions of aqueous nitric acid, or they may be transferred with rinsing into a clean separatory funnel. Three extractions with 20 to 30 ml each of 0.5 M, 4 M, and 0.5 M nitric acid were used to reextract the uranium into an aqueous solution.

B. Extraction and Measurement at the Microgram Uranium Level

When operating at the microgram level, a solution of uranium-233 (10^{-7} to 10^{-8} g) together with about 20 μg of natural uranium (as sulfate) was submitted to reductive extraction with cupferron for about 50 to 60 min in the modified cell. The uranium (IV/III) cupferrate was then reextracted in cell D from the ether solution into three successive 15 ml portions of 7 M nitric acid. The combined nitric acid extract (about 50 ml) was evaporated to about 5 ml volume, treated with 25 to 30 ml of concentrated nitric acid and 2 ml of perchloric acid and was then evaporated to dryness. The residue was digested with about 10 ml of 0.1 M nitric acid for a few minutes; the solution obtained, after addition of about 10 μg. more of natural uranium carrier (as sulfate), was used for electrodeposition of the uranium onto a platinum planchet from an oxalate medium (14). A windowless flow counter with Q-gas was used for counting the alpha emission from the electrodeposited uranium (14).

The whole operation took about 4 to 5 hours. Each measurement of alphas from the samples was calibrated by counting a uranium oxide standard (National Bureau of Standards, No. 836-5).

V. RESULTS AND DISCUSSION

A. Uranium Recovery at the Milligram Level Using Photometric Measurement

The ferrocyanide colorimetric procedure in 0.05 N nitric acid (11, pages 100 to 102) was used to evaluate uranium recovery at the milligram level (Table I). The organic matter in the final nitric acid extract must be destroyed by an initial evaporation with nitric acid and a second evaporation with nitric and perchloric acids with the solution being finally taken to dryness. No significant amount of sulfate ion may be present or erroneously low results will be obtained.

In the first two runs of Group I in Table I no attempt was made to destroy organic matter. When it was recognized that enough undecomposed cupferron remained in the aqueous layer to jeopardize the colorimetric procedure, wet oxidations with nitric, perchloric and sulfuric acids were employed. In Runs 3 through 7 the aqueous solution was fumed with 2 ml of concentrated sulferic acid to a volume of about 2 ml. The diluted solution (20 to 30 ml) was neutralized with sodium hydroxide and was then made about 0.05 N in free nitric acid. On the suspicion that sulfate was bleaching the uranyl ferrocyanide color, the solution in Run 8 was fumed until only a moist residue remained containing not more than 0.2 ml of acid. The apparent yield determined from colorimetric measurement rose from 20 to 70%. Realizing that 2 ml of sulfuric acid forms 5.5 g. of sodium sulfate, this amount of salt was added to a 2 mg uranium sample which was checked colorimetrically. The optical density corresponded to about one-fifth of the appropriate value on the calibration curve. The uranium recoveries for the first eight runs of Table I are consequently estimated on the basis of this correction. In one run substitution of a spiral platinum cathode for the mercury pool gave an estimated recovery of only 75%.

The second set of twelve runs (Group II of Table I) was conducted in an identical manner, except that during the destruction of the residual organic matter the samples were taken to dryness with perchloric acid and no sulfate was added. In three runs the complete double cupferron procedure was tested; the uranyl solutions were first twice extracted with 12 ml portions of chloroform containing cupferron (250 mg/50 ml), followed by a 10 ml chloroform wash, and then electrolyzed, extracted with ether cupferron solution and reextracted into nitric acid solution. The average recovery for these three runs was 85%. The overall uranium recovery was also checked by the spectrophotometric 8-quinolinol procedure (12) in four of the runs of Group II. The residue, after destruction of organic matter in the original nitric acid extract of uranium cupferrate was taken up with water (8 ml) and the pH was adjusted to 8.0 with 1 M sodium hydroxide and 1 M hydrochloric acid. The solution was transferred to a separatory funnel; the beaker was rinsed with 25 ml of buffer solution of pH 8.0 (1 M ammonium chloride with ammonia added to pH 8.0), which was also added to the separatory funnel. Then 20 ml of a solution of 1% oxine in chloroform was added and the mixture shaken for 6 to 8 minutes. The chloroform layer was withdrawn, and the aqueous layer was washed with two 5 ml portions of chloroform. The combined chloroform extracts were diluted to 100 ml with chloroform and the absorbance measured at 430 mu, using matched 1 cm Corex cells, in a Beckman DU spectrophotometer. The blank solution was prepared by extracting 20 ml of 1% oxine solution in chloroform with 25 ml of the buffer solution of pH 8, followed by a wash with two 5 ml portions of chloroform and dilution of the chloroform extracts to 100 ml with chloroform. From the measured absorbance values, the corresponding uranium concentration was obtained from a calibration curve (12).

A few experiments were attempted (Group III of Table I) in which

an internal platinum anode was used; potentials from -1.2 to -2.5 volt were tried. The poor uranium recovery (ferrocyanide method) indicates that re-oxidation of the uranium occurs at an internal anode and that this modification is not feasible.

B. Uranium Recovery at the Microgram Level Using Tracer Technique

The results of applying the procedure to samples containing about 30×1.0^{-6} g of natural uranium as carrier and 3×10^{-8} to 13×10^{-8} g of uranium-233 as tracer are given in Table II; the average uranium recovery as measured by alpha counting was 85.8 ± 1.3%. In calculating the recovery of the uranium-233 tracer for Table II (as also in the following Tables III, IV and VI), a correction has been applied for the alpha activity of the natural uranium carrier based on 0.75 c.p.m. per μg of natural uranium (4) at 50% geometry.

In one run (7×10^{-8} g uranium), the uranium-233 together with 20 μg of natural uranium carrier in 10 ml of 1% sulfuric acid was first extracted twice with 12 ml portions of chloroform containing cupferron (250 mg/50ml) followed by a 10 ml chloroform wash.

In order to locate where the 9% loss in these runs (a loss of about 6% is known to be ascribable to the electrodeposition step prior to counting) was occurring, several material balance runs were undertaken. After the regular electrolysis and extraction procedure using 20 μg of carrier was completed, the catholyte, the cathode compartment and the bridge compartment walls, and the residual ether-cupferron phase from the final nitric acid extraction were checked as follows for uranium activity.

(1) The catholyte was siphoned off and decomposed by evaporation with nitric and sulfuric acids. The residue was dissolved and, after the addition of 10 μg of natural uranium, was electroplated and counted as usual.

(2) After removing the catholyte, about 20 ml of saturated ammonium oxalate solution was poured into the cathode compartment over the mercury and the solution was stirred for an hour. The bridge compartment, B, meanwhile, was kept filled with ammonium oxalate solution. After an hour, the mercury was carefully withdrawn, and the solutions from the cathode and bridge compartments were transferred to an electroplating cell; after addition of 20 μg of natural uranium as carrier and adjustment of pH, electrodeposition and counting were done as usual.

(3) The residual ether-cupferron phase from the 7 M nitric acid extraction was transferred to a small conical flask, carefully evaporated on a hot plate (temperature controlled by a Variac) and, after decomposition with nitric and perchloric acids, electroplated with 10 μg of added carrier and counted.

It is apparent from the data for these material balance runs (Table III) that there is about 4 to 6% loss in the residual catholyte and about 2 to 3% loss in the residual ether-cupferron phase. Thus, about 93% of the total uranium activity could be traced. The final electrodeposition step alone for uranium-233 (in the presence of carrier), as reported previously (14), affords a 94% recovery of uranium.

C. Effect of Carrier on Uranium Recovery

To determine the influence of the carrier on uranium recovery, experiments were performed which followed essentially the same procedure as already described, except that in one run about 10 μg of carrier was added before extraction and another 10 μg of carrier was added before electrodeposition, and in other runs, no carrier at all was added. The data are summarized in Table IV. The calculations were made by comparing the activity of sample plates obtained after electrodeposition with the activity of a platinum disk prepared by evaporating 1 ml of stock

uranium-233 solution on it and then igniting to uranium oxide. It is evident from these results that the presence of 20 μg of carrier enhances the uranium recovery.

D. Recovery (Decontamination) of Uranium from Mixed Fission Products

In order to ascertain how fission products would behave with respect to the proposed reductive extraction procedure, a few carefully monitored runs were made, following the flowsheet outlined in Figure 3. At appropriate locations in the procedure, alpha, beta and gamma activities were measured. The results, in terms of the percentage of the total activity taken for that particular experiment, are given in Table V-A.

In two of the runs the preextraction of the unreduced solution with cupferron was omitted and 10 μg of natural uranium was added as a carrier. The original 25 ml solution (1% in sulfuric acid) was submitted to reductive extraction with cupferron, followed by addition of 10 more μg of uranium carrier and electroplating. The activities, in terms of percentage of total activity taken, are shown in Table V-B for the residual catholyte after extraction, the residual plating solution after electrodeposition, and the final plate.

From a comparison of the data in sections A and B of Table V, it may be deduced that:

(1) About 20% of the fission product gamma activity and 1.3% of its beta activity are removed by the preextraction step.

(2) Approximately 0.9% of the fission product alpha activity goes through the separation scheme (this quantity is logically attributable to alpha-emittive uranium present in the fission products).

(3) Apparently the only major contamination of the uranium resulting from omission of the preextraction step (for this particular batch

of fission products)is the 1.3% beta activity.

Since only about 0.9% of the fission products (on the basis of counting alphas) can be plated after reductive extraction with cupferron in ether and since a recovery of 85.8 ± 1.3% was found for microgram quantities of uranium, it would appear that uranium can be recovered from admixture with gross fission products and then determined by the proposed method. This was examined by the following procedure: 7×10^{-8} g of uranium-233 together with about 10 μg of natural uranium carrier was mixed with increasing amounts of fission products to give an aqueous phase whose total volume (1% in sulfuric acid) was about 30 ml. The procedure of reduction, extraction and plating was the same as before. The results are tabulated in Table VI.

The uranium recovery figures (last column) are corrected for carrier activity as in all previous such runs. An average of 0.9% recovery was assumed for fission product alpha-activity (Table V) and this correction is also applied. From these results it follows that uranium-233 can be separated in about 85% yield from a mixture with gross fission products. Presumably, even more disproportionately large ratios of fission activities to uranium might be adequately separable by this technique. This point is difficult to test rigorously, however, because of the sizeable correction necessary for the alpha activity of the available fission product material. It is interesting to note that the average recovery in the presence of fission products (Table VI) checks well with the recovery found in their absence (Table II), but the scatter of the data is greater, consequent to the larger corrections applied (85.0% ± 8.0% and 85.8% ± 1.3%, respectively).

VI. EVALUATION OF THE PROCEDURE

From the theoretical and manipulative viewpoints, the most important advance in the procedure developed is the introduction of an electrolytic process for changing the oxidation state of uranium in solution without introducing reagents or manual operations. In addition, a relatively simple one-piece glass apparatus was devised which permits the preextraction, the electrolysis, the uranium extraction by cupferron-ether, and the reextraction of the uranium from the ether to aqueous nitric acid solution to be carried out with a minimum number of operations, and which can be readily adapted for remote-control operation.

Experiments on milligram quantities of uranium, using the colorimetric ferrocyanide and the spectrophotometric oxinate procedures to evaluate the overall uranium recovery, indicate the essentially quantitative character of the reductive extraction procedure, with a transport of uranium that is at least 94.0 $\pm$ 1.5% complete. Runs which included preextraction of the aqueous uranium (VI) solution with cupferron in chloroform established the nonextraction of uranium by this step.

The extrapolation from milligram to microgram and submicrogram levels was tested with uranium-233 solutions by the complete process for uranium isolation involving preextraction with cupferron, simultaneous electrochemical reduction and cupferron extraction of the uranium, reextraction of the uranium into nitric acid, destruction of organic matter, electrodeposition of the uranium and alpha counting. The recovery or yield, based on comparison of the alpha count of the uranium-233 taken and of the final plate obtained, was 85.8 $\pm$ 1.3% for amounts of uranium-233 of the order of from 10^{-7} to 10^{-8} g initially in 30 ml of solution, to which was added 20 micrograms of natural uranium as carrier. The recovery in the plating

process was 94% or better. The remaining 9% loss was traced to losses of about 5% in the residual aqueous layer after extraction and of about 3 to 4% in the residual ether layer after extraction with nitric acid.

The whole operation takes about 4 hours. It should be noted that although an average recovery of 94% characterizes the final plating step at the microgram level, the reductive-extraction and subsequent extraction steps are presumably equilibrium processes whose yield could be brought up to about 100% if the duration of reduction and the numbers of extractions were increased. It is probable that with a total operating time of 5 to 6 hours, the overall average recovery could be raised from 85% to 94%.

The low recovery obtained is satisfactory at the milligram to submicrogram level since it is reproducible and, after correction for loss, would permit an accuracy good to at least 10% at the microgram level and about 2% at the milligram level.

It was considered that the extent to which radiochemical contamination by active nucleides could be removed from the final uranium plate would provide a sensitive measure of the success of the separation scheme.

Orientation studies showed that only about 1% of the alpha activity in the mixed fission products (which is logically attributable to the uranium present) is transmitted through the procedure and is finally recovered on the planchet used for counting. This result, in combination with radioactivity balance studies in which the distribution of the original alpha, beta, and gamma radiation present was followed in order to see where separation was occurring in the various steps of the procedure, indicated that uranium can be separated from a fission-product sample.

The procedure was then applied to the recovery of uranium-233 (about 7×10^{-8} g), when present in admixture with an appropriate quantity of natural

uranium carrier and increasing amounts of fission products mixture; the maximum ratio of the latter to uranium-233 was set at a point beyond which contamination problems would be serious. The average recovery, based on the alpha count of the final plate, was 85.0 ± 8.0%. This figure compares nicely with the yield of 85.8 ± 1.3% reported for pure uranium solution.

The several stages of separation used in the present procedure, i.e., removal of elements in the preextraction stage, reduction of elements into the mercury cathode, removal of uranium in the reductive extraction step, transfer of uranium from ether to aqueous nitric acid and the electrodeposition step, plus the selectivity of the photometric or radioactive counting measuring step, should provide the desired specificity for uranium in the presence of other elements.

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Table I. Recovery of Uranium at the Milligram Level by Reductive-Extraction with Cupferron

Group	Number of Runs	Uranium Taken mg.	Electrolysis Duration min.	Uranium Recovery
I	8	2 to 9	30 to 160	100% ± 20%
II	12	0.1 to 4	50	94.0% ± 1.5%
III	7	1 to 2	50	43% (average)

Table II. Recovery of Uranium at the Microgram Level by Reductive-Extraction with Cupferron and Subsequent Electrodeposition

(30 μg. of natural uranium carrier present)

Uranium-233 Taken g.	Recovery Based on Counting %
3×10^{-8}	74
7×10^{-8}	86, 84, 87, 86
	85, 87, 83
13×10^{-8}	88
Average Recovery*	85.8 ± 1.3%

* First run omitted.

TABLE III. MATERIAL BALANCE RUNS FOR URANIUM RECOVERY USING URANIUM-233 TRACER

Uranium-233 Taken g.	Uranium Recovery* %	% Uranium Activity In		
		Residual Catholyte	Cathode and Bridge Compartment Walls	Residual Ether-Cupferron Phase
7×10^{-8}	85.3	4	0	3
7×10^{-8}	84.3	6	0	2
7×10^{-8}	86.4	5	0	2

* There is a loss of 6% in the final electrodeposition step prior to counting.

TABLE IV. URANIUM RECOVERY USING URANIUM-233 TRACER: EFFECT OF CARRIER

Uranium-233 Taken			Natural Uranium Carrier g.	Uranium Found	
No.	g.	Activity counts/min		Activity counts/min	Recovery %
1	7×10^{-8}	810 ± 29	Nil	560 ± 24	69
2	7×10^{-8}	810 ± 29	Nil	520 ± 23	65
3	7×10^{-8}	810 ± 29	20×10^{-6}	710 ± 27	86

TABLE V. EFFECT OF FISSION PRODUCTS ON THE PROPOSED PROCEDURES*

A. Recovery of Fission Products by Electroplating after Preextraction and Reductive Extraction With Cupferron in Ether (1 ml of Fission Products Solution Added**)

No.	Activity in Aqueous Phase (A)	(B)	Activity in Ether Phase: Plate (C) α	β	Residual Plating Solution (C') γ	Activity of Plate for Counting α	β
1	79%	72%	0.84%	0%	9.5%	1.12%	0%
2	86%	70%	0.80%	0%	7.5%	0.98%	0%

B. Recovery of Fission Products by Electroplating After Reductive Extraction With Cupferron in Ether (No Preextraction)

No.	Fission Products Taken** ml	Natural Uranium Carrier Taken μg	Activity in Residual Catholyte γ	Activity in Residual Plating Solution γ	Activity of Plate α	β
1	1	20	92%	4%	0.83%	1.5%
2	2	20	90%	5%	0.94%	1.1%

* The letters in parentheses refer to the sampling locations noted in Figure 3.

** 1.00 ml of fission products solution gives 9207 ± 97 α counts/min., 1707 ± 61 β counts/min. and 1890 ± 44 γ counts/min.

TABLE VI. SEPARATION OF SUBMICROGRAM AMOUNTS OF URANIUM-233 FROM GROSS FISSION PRODUCTS

(20 μg of natural uranium added as carrier)

Run No.	Fission Product Solution Taken* ml	Uranium-233 Taken μg	Uranium-233 Taken Alpha Activity counts/min	Residual Catholyte γ Activity	Activity of Plate α counts /min	Activity of Plate β % Recovery	Uranium-233 Recovered - %
1	1	0.07	500 ± 10	90%	500 ± 22	0.9%	80.4
2	1	0.07	500 ± 10	93%	510 ± 23	1.2%	82.5
3	5	0.07	500 ± 10	96%	825 ± 29	1.0%	79.0
4	5	0.07	500 ± 10	94%	800 ± 28	1.5%	74.0
5	10	0.08+	600 ± 11	94%	1440 ± 38	2.3%	99.8
6	10	0.08+	600 ± 11	95%	1410 ± 38	1.8%	94.2

* 1.00 ml of fission products solution gives 9207 ± 97 α counts/min, 1707 ± 61 β counts/min, and 1890 ± 44 γ counts/min.

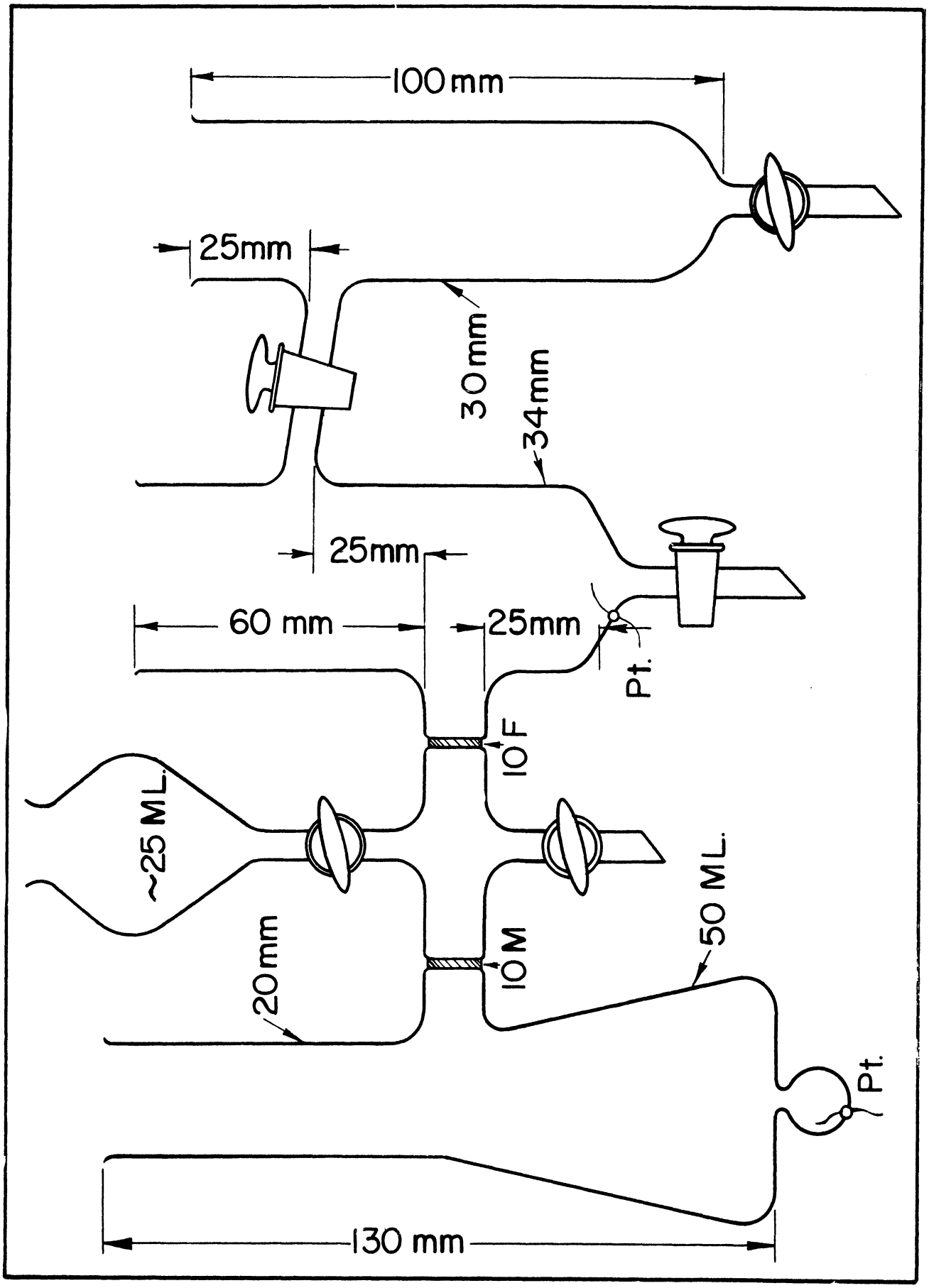

Fig. 1 Apparatus for the Simultaneous Reduction and Extraction of Uranium. All stopcocks are Corning No. 7320.

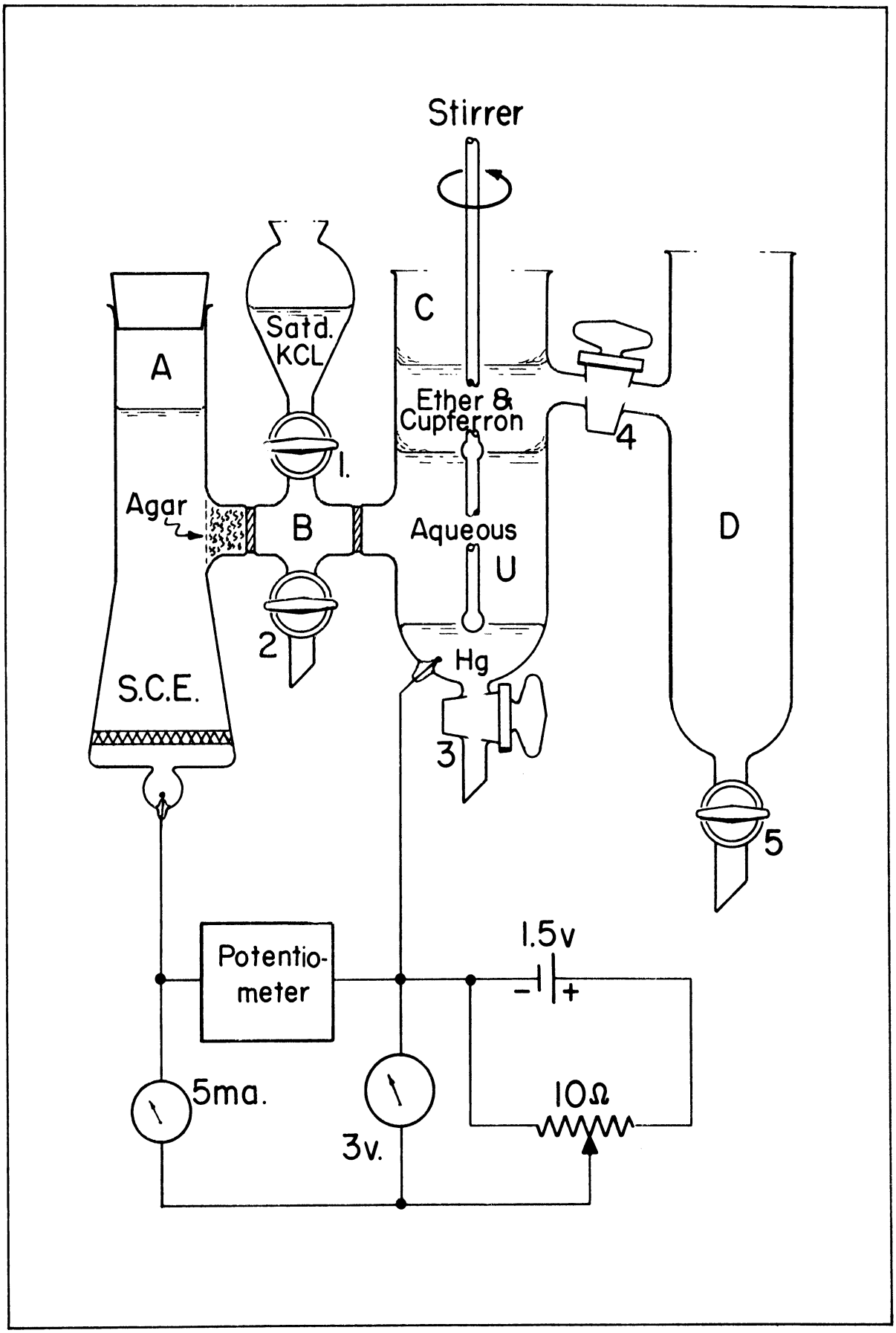

Fig.2 Electrical Circuit for the Electrochemical Reduction of Uranium

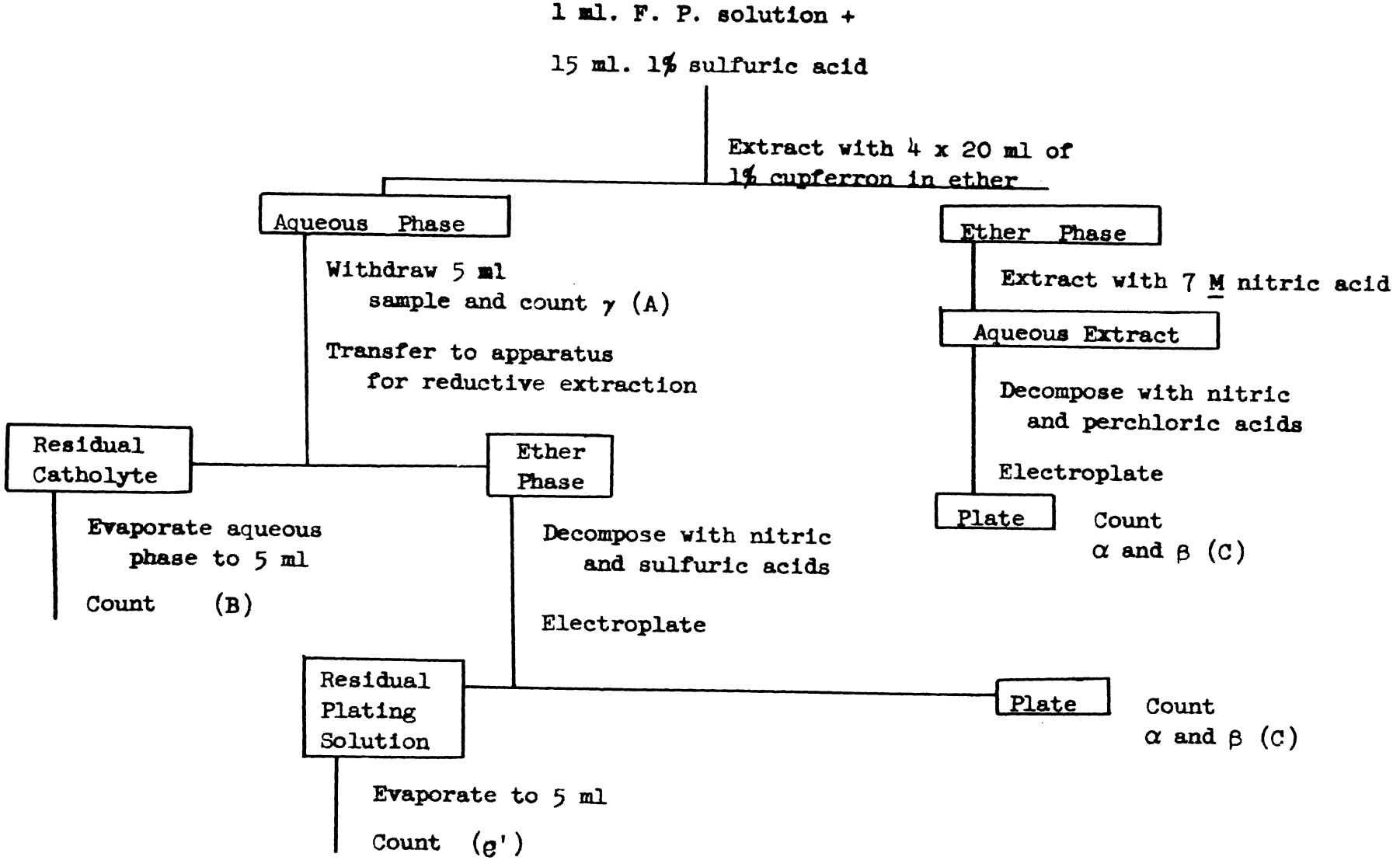

Figure 3. Procedure Followed in Determining the Distribution of Fission Products (F. P.) in the Proposed Method for Recovering Minute Amounts of Uranium

(The letters in parentheses are sample designations)