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ELECTROANALYSIS OF COBALT, NICKEL, AND COPPER IN PLUTONIUM SOLUTIONS WITH A MERCURY CATHODE

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CHEMISTRY TRANSURANIC

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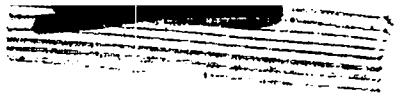

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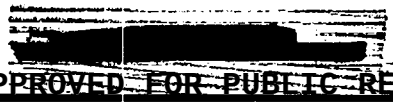
ABSTRACT

Equipment and analytical procedure have been described for the analysis of cobalt, nickel, or copper in the presence of plutonium by electrodeposition on a mercury cathode. Only submicrogram quantities of plutonium remain with the amalgam which is formed. The analyses of some binary plutonium alloys of these metals are reported.



ELECTROANALYSIS OF COBALT, NICKEL, AND COPPER IN PLUTONIUM SOLUTIONS WITH A MERCURY CATHODE

INTRODUCTION

Mercury has been used as a cathode in electrochemical analyses for many years.[1, 2] It is almost the only metal that possesses, under certain circumstances, some advantages over platinum. Frequently, mercury cathodes have been employed for removing zinc and other metals below zinc in the electromotive series, leaving in solution for further analysis such elements as aluminum, magnesium, titanium, vanadium, or uranium.[3] At other times, the mercury cathode, either as an amalgamated brass electrode[4] or as the liquid metal,[5] has been utilized in the determination of such elements as zinc, lead, bismuth, or antimony by weighing the electrodeposited metal. In either case, the advantage associated with the use of mercury cathodes is the relatively high acid concentration permitted in the electrolysis solution, due to the high overvoltage of hydrogen on mercury. Also, if the deposited metal forms an amalgam, the metal is thereby somewhat protected from the dissolving action of the acid. Other characteristics of the mercury cathode and the proper conditions under which

it finds successful applications have been fully reviewed by Bottger[6] and Sands.[7]

The possibility of maintaining relatively strong acid conditions during electroanalysis is especially significant when dealing with solutions containing plutonium. Many compounds of this element undergo hydrolysis into insoluble products even at low pH values. To prevent precipitation of the plutonium before or during electroanalysis, the solution must be approximately 0.1 N with respect to some strong acid. Because of such requirements, the electroanalysis of copper, cobalt, and nickel in solutions that also contain plutonium was investigated, using liquid mercury as a cathode. The work described in this Report was in progress from March, 1947 to April, 1949.

Conditions for analysis were selected with the thought that samples would contain 10 to 20 mg of the metal under determination. No preliminary separation of plutonium, such as by peroxide precipitation, was planned. This meant that a rigid control of the spray produced during electrolysis was essential, since samples may contain as much as 100 to 200 mg of plutonium in 10 ml of solution. At the same time, attempts were made to employ equipment and procedures that are the least complicated and can be used by relatively inexperienced analysts.

Health-Safety Rules of the Laboratory, for protection from radioactive material, must be strictly followed in employing any of the following procedures.

APPARATUS AND REAGENTS

In preparing the necessary equipment for electroanalysis with a mercury cathode, two factors were considered: (1) the prevention of plutonium contamination, especially from spray produced during electrolysis, and (2) a minimum weight for the cathode cell and mercury to permit maximum accuracy in weighing.

The mercury cell was made from a standard taper 24/25 Pyrex outer joint by closing the tube at the end opposite the standard taper with a test-tube end, giving a total length of 8 cm (Figure 1). A short length of 0.010-inch diameter platinum wire was sealed through this bottom end of the cell to make electrical contact with the mercury cathode. During use, the cell was closed with a standard taper 24/25 Pyrex inner joint which was narrowed and connected to a short length of 7 mm-diameter capillary tubing directly above the standard taper (Figure 1). This served to center the 0.030-inch diameter platinum wire that supported the

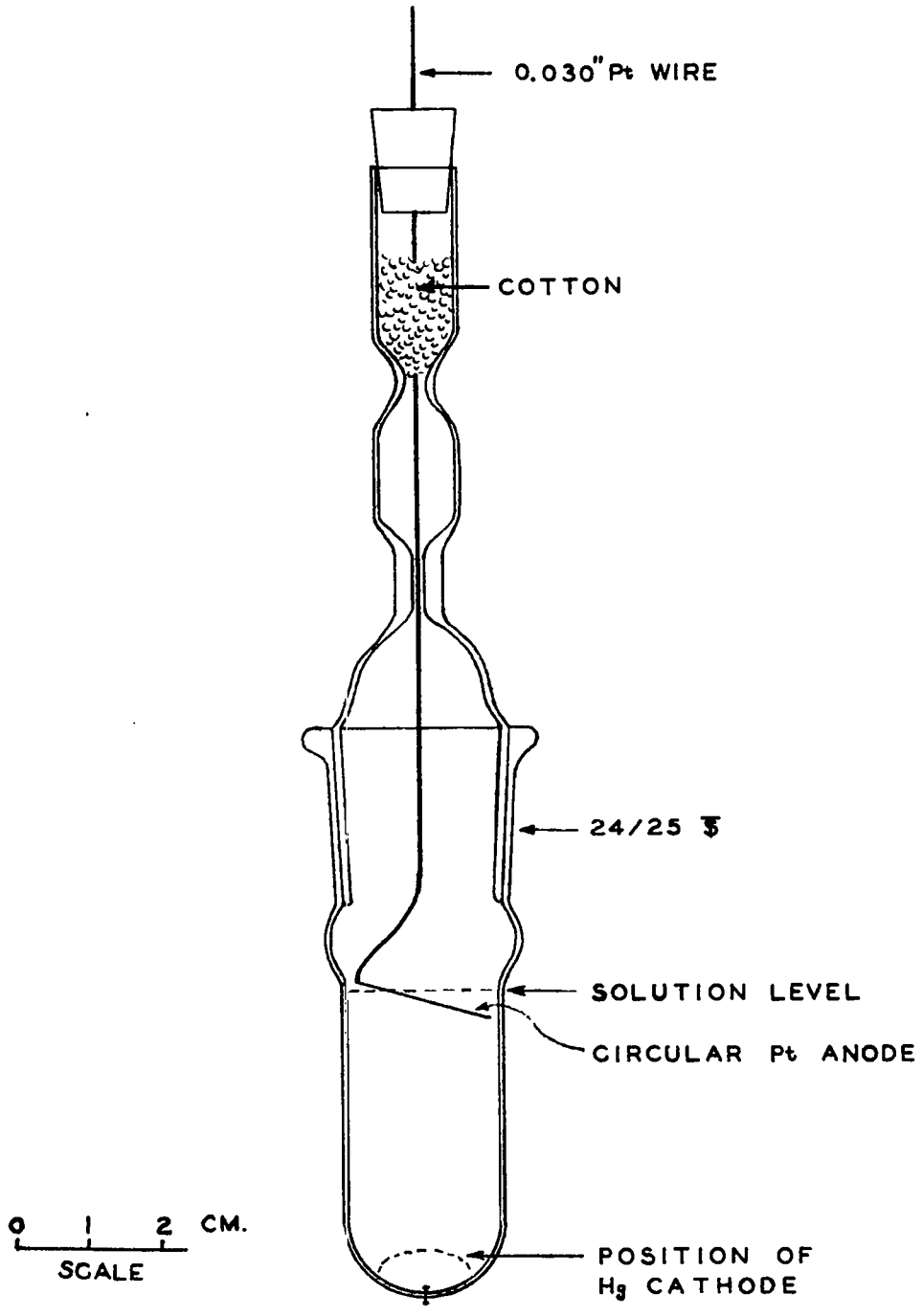


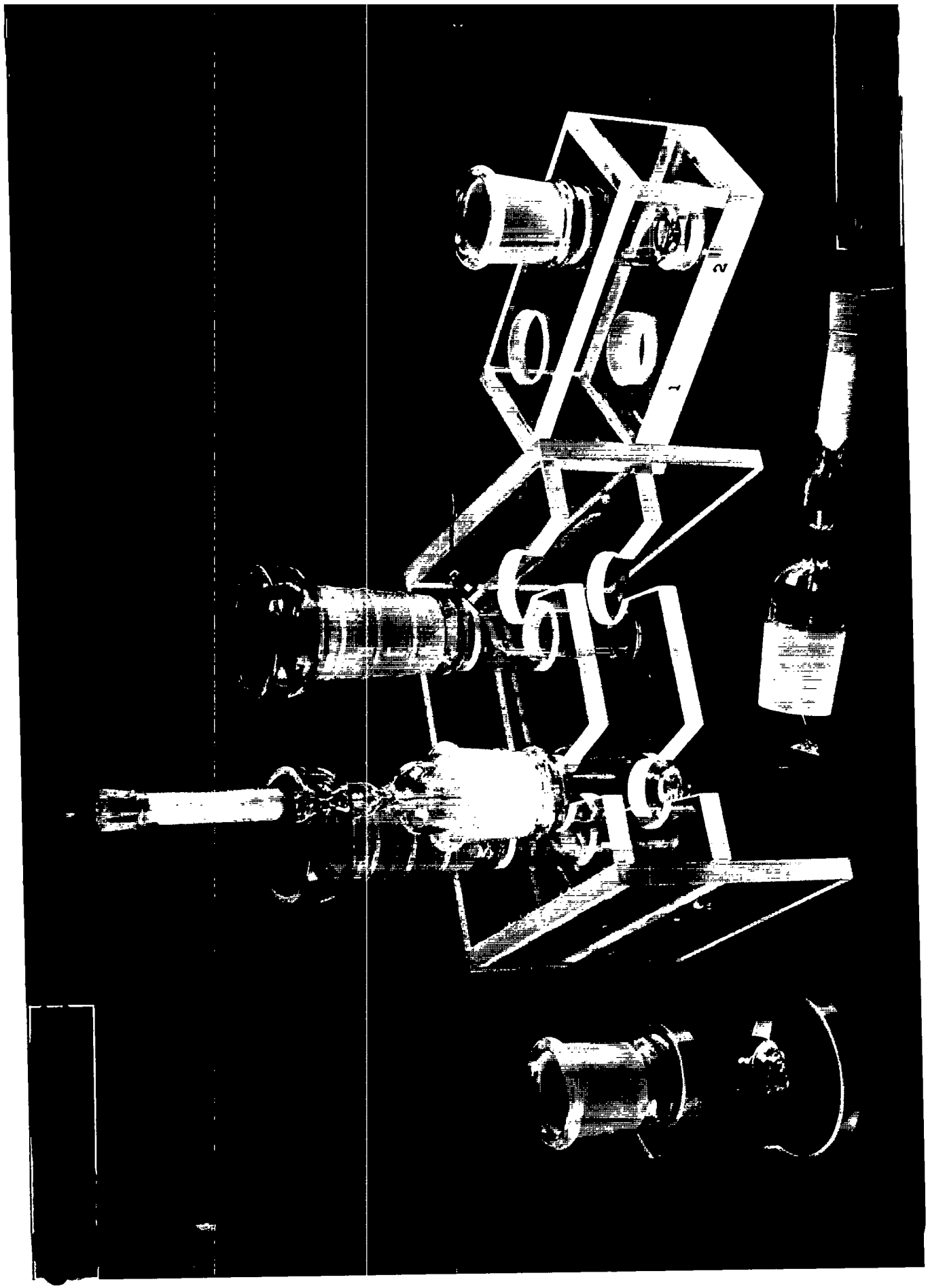
FIGURE 1.

APPARATUS FOR ELECTROANALYSIS WITH MERCURY CATHODE

circular anode. The anode was a 0.005-inch thick platinum disc with a diameter of about 1.6 cm. The capillary tube was connected with a 5-cm length of 12-mm tubing, narrowed in the middle to hold a small wad of cotton. The anode-supporting platinum wire was held in position with a cork stopper through the center of which the wire had been inserted.

Several mercury cathode cells, the upper platinum anode-supporting tubes, and various cell holders are shown in Figure 2. During weighing and drying, the mercury cathode cells were placed in an aluminum holder (shown to the left in Figure 2) which was cut from a 2-inch length of 2-inch diameter tubing. For holding the anode units when not in use and for collecting rinsings from these units, a mercury-seal type of standard taper 24/25 Pyrex outer joint, sealed at the bottom with a test-tube end, was used. These joints are shown in the back part of the central support in Figure 2. This same support was used to hold the cathode cell during electrolysis and has platinum contacts in its underneath section which touch the platinum wires on the bottom of the cathode cells when they are in place.

An Ainsworth balance, type TC, was used for making all weighings by the method of short swings.



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Using the procedures for weighing and determining the sensitivity as described by Benedetti-Pichler,[8] the average deviation of a single weighing with loads from 0 to 50 grams was 0.01 mg. Variations in room conditions were probably more responsible for errors in weighing than was the performance of the balance. A tare consisting of an aluminum holder and an empty cathode cell was always used in weighing, so that only weights corresponding to the 3 to 10 grams of mercury were required.

Reagent-grade or CP chemicals were used without further purification. A solution of plutonium, prepared by dissolving a sample of the pure metal in 6 N HCl and containing 11.8 mg Pu per ml at final dilution, was used for all work involving this element, other than plutonium alloy samples.

PROCEDURE

The following general procedure was used; such changes as were made for special circumstances are described in the section dealing with experimental results.

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Carefully clean the mercury cathode cell with warm concentrated nitric acid and rinse thoroughly with distilled water. Add 3 to 10 grams of the best reagent-grade mercury to the cell for each determination. It is essential that the cell be scrupulously clean and that the mercury be of the purest grade possible. The quantity of mercury depends upon the nature and amount of metal to be deposited. The sample should contain at least 10 to 20 mg of the metal and may contain 100 to 200 mg of plutonium.

Prepare the clean cell, containing mercury, for use by washing once with a 5-ml portion of 1 N H_2SO_4, three times with distilled water, and twice with acetone. After the addition of each portion of wash liquid, agitate the cell and contents with a circular motion, holding the cell at a slight angle with an ordinary metal wire test-tube clamp. Remove the wash liquid by suction with a glass tube drawn to a fine tip, taking extreme care that no mercury is removed. After withdrawing most of the acetone, continue drawing air into the cell with the suction tube and gently agitating the mercury until all remaining acetone evaporates. Too vigorous agitation must be carefully avoided at all times, since, it causes difficulty in removing the water and acetone that may remain underneath the mercury.

Wipe the cathode cell first with a moist cloth which must be free of loose fibers and then with a reasonably dry chamois.[9] Place the cell in an aluminum holder in the balance case for 30 to 45 minutes, and then weigh to 0.01 mg by the method of short swings.

Before electrodeposition, anions other than sulfate should be removed from the sample by evaporation with sulfuric acid to SO_3 fumes. After this preliminary treatment, transfer the sample to the weighed cell, together with sufficient sulfuric acid to make the final volume of 10 ml about 0.5 N. Dilute with water to bring the solution level to the position indicated in Figure 1. Insert the anode unit into the cell, with the platinum anode at a 15° angle to the horizontal and its upper end just above the solution level. This position of the solution level and anode tends to minimize the spray produced during electrolysis. Place the cell in the holder that permits making electrical contact with the electrodes, and begin deposition.

Current for the electrolysis can be supplied by two 6-volt storage batteries connected in series. Begin electrodeposition at a rate of 0.1 ampere or less, at 5 to 6 volts, with the electrodes separated by about 3.5 cm, and continue for 10 to 30 minutes. During this period, the plutonium will be reduced to

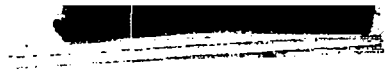
the trivalent state, if it has not been added in this form, and most of the metal will be deposited with a minimum loss of sample by spray. Then increase the current to about 0.4 amperes for ten minutes. During this time, it may be advisable to remove the cell from the holder by lifting it with a test-tube clamp and gently rotating it at an angle so that spray collected on the glass wall above the anode will be rinsed back into the electrolyte. Finally, decrease the current to 0.01 to 0.02 amperes for a few minutes to reduce the amount of spray before opening the cell and to allow the cell and contents to cool.

Disconnect the cell from the source of current, remove the clip from the platinum wire at the top of the anode unit, and raise this unit until above the cathode cell. Briefly rinse the platinum anode with 1 N H_2SO_4 into the cell and then set aside the anode unit in one of the mercury-seal type standard taper joints at the back of the cell holder. Immediately withdraw by suction as much as possible of the electrolyte from the cathode cell without risking loss of any mercury. It may be desirable to collect this solution removed by suction and the first sulfuric acid rinse that follows in a flask separate from the other rinses, since the first two will contain

practically all of the plutonium from the original sample. Quickly rinse the inside of the cell with a 5-ml portion of 1 N H_2SO_4, agitate the cell carefully, and remove this rinse solution by suction, again using a glass tube drawn to a fine point. Repeat this rinsing process with another 5-ml portion of 1 N H_2SO_4, three times with water, and twice with acetone. At this point, follow the same procedure for drying the cell, wiping and placing it in the balance case, as was described above for the preparation of the clean cell before beginning electrodeposition. Weigh the cell and contents to the nearest 0.01 mg. The mercury used as a cathode should be discarded and the cell cleaned before making another determination.

EXPERIMENTAL RESULTS AND DISCUSSION

Since the standard potential in aqueous solution for the plutonium couple Pu(metal)-Pu(III) is +2.13 volts,[10] it was not expected that metallic plutonium would be even partially formed on the mercury cathode. However, at first, only microgram quantities of the active element were added to solutions



of nickel and cobalt in depositing these metals on mercury. Using the electroanalysis equipment that has been described, with samples containing about 20 mg of metal and 14 micrograms of plutonium (when this element was added), the results listed in Table I were obtained.

Table I

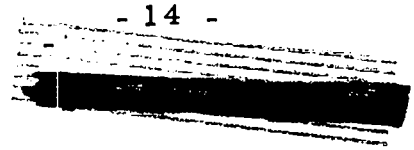
EFFECT OF PLUTONIUM ON ELECTROANALYSIS OF NICKEL AND COBALT

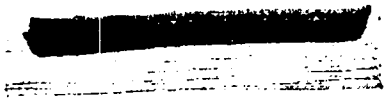
Nickel*		Cobalt**	
No Pu Added	Pu Added	No Pu Added	Pu Added
19.69 mg	19.83 mg	19.92 mg	19.98 mg
19.58	19.77	20.06	
19.76	19.82	19.99	
19.70		20.12	
19.71		20.11	

*Volume aliquots, equal to those used for above electroanalyses, showed 19.69 ± 0.01 mg Ni by gravimetric analysis.

**Volume aliquots analyzed gravimetrically showed 20.13 ± 0.06 mg Co.

The procedure was changed to the extent that anhydrous ethyl alcohol and ether were used at times in place of acetone. Equal-volume aliquots of 10 ml were taken from the standardized solutions of nickel and cobalt sulfate as samples for each





deposition. These first results gave some indication of the accuracy that might be expected from the equipment and procedure used, as well as verification of the fact that plutonium does not interfere.

Some of the mercury in the cathode cell, after several deposition experiments, was dissolved by addition of a small volume of nitric acid. This acid salt solution was withdrawn from the cell and was found to contain only 0.003 microgram of plutonium by radiochemical assay.[11] In addition to these analyses of samples containing nickel and cobalt, two preliminary electrodepositions were made with portions of a standardized copper sulfate solution with results similar to those shown in Table I. The weights of copper found were 20.03 and 20.03 mg, compared with the known amount added of 20.11 mg.

When it became necessary to analyze some plutonium-cobalt alloys of unknown composition, preliminary separation of most of the plutonium by peroxide precipitation was included at first as part of the alloy analysis. The results are reported in Table II.

[redacted]

Table II

ANALYSIS OF PLUTONIUM-COBALT ALLOYS BY ELECTRODEPOSITION

Alloy No.	Sample Weight	Cobalt Weight	Percent Weight
1	99.9 mg	1.95 mg	1.95 %
	111.5	2.10	1.88
	101.0	1.81	1.79
	108.0	2.04	1.89
2	91.1	5.48	6.02
	108.4	6.69	6.17
3	114.1	2.02	1.77
	122.9	2.29	1.86
4	91.4	0.26	0.28
	94.2	0.16	0.17

There was no difficulty in dissolving the Pu-Co (and later Pu-Ni) alloys in 6 N HCl. Precipitation of the plutonium was made in centrifuge cones in solutions that were 1 N HCl, 0.2 N H_2SO_4, and 10% hydrogen peroxide.[12]

Before transferring to a mercury cathode cell, the combined supernatant liquid and rinses were evaporated to SO_3 fumes with enough sulfuric acid to give a final concentration of 0.5 N H_2SO_4 in the 10 ml of sample. The agreement between duplicate and quadruplicate results in Table II is the only indication of a correct analysis of these alloys.

[redacted]

Before analyzing other alloy samples for which a preliminary plutonium peroxide separation was not planned, two known samples containing 2.02 mg of cobalt were electroanalyzed in the presence of 95 mg of plutonium. These analyses gave 2.03 and 2.07 mg of cobalt, revealing that plutonium in this amount does not interfere. Again, the mercury after deposition was partially dissolved in nitric acid; radiochemical assay of this mercuric nitrate solution disclosed that less than 0.001 microgram of plutonium remained in the deposition cell.

Two other plutonium alloys were analyzed, but without first separating any of the plutonium which varied between 5 and 26 mg. The results are given in Table III. It was not possible to dissolve the copper alloy in hydrochloric acid alone; but when several drops of concentrated nitric acid had been added to 1 ml of 12 N HCl in contact with the Pu-Cu alloy, dissolution was complete within half an hour. A very slight amount of black residue was taken into solution after the sample had been treated with sulfuric acid and taken to SO_3 fumes.

Table III

ANALYSIS OF Pu-Co AND Pu-Cu ALLOYS

Alloy	Sample Weight	Weight of Metal	Percent Metal
Pu-Co No. 5	22.6 mg	1.49 mg	6.59 % Co
	23.3	1.60	6.87
	26.1	1.75	6.70
	27.7	1.82	6.57
Pu-Cu No. 1	28.52 mg	21.58 mg	75.67 %
	22.70	17.07	75.20
	25.04	18.81	75.12
	25.84	19.50	75.46

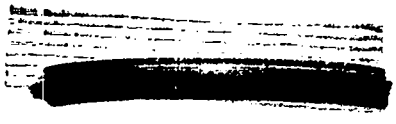
Again, the composition of these two alloy samples was not known prior to making the determinations. However, an independent analysis of copper was made on another portion of the Pu-Cu alloy No. 1; the copper was separated from the plutonium as cuprous thiocyanate and then determined iodometrically.[13] The average of five volumetric determinations, 75.46 ± 0.16 percent Cu, is in good agreement with the average of the results listed in Table III, 75.36 ± 0.20 percent Cu. Radiochemical assay of a properly diluted aliquot for plutonium in a portion of Pu-Co alloy No. 5 was found to give 93.4 and 92.3 percent Pu. This agrees reasonably well, for this type of analysis, with the average of the four electrochemical determinations, 6.68 ± 0.10 percent Co, in Table III.

One other plutonium-copper alloy was analyzed by electrodeposition on a mercury cathode. Starting with a sample weight of 0.3192 g, deposition of 0.2605 g of copper was obtained on about 10 g of mercury. The supernatant liquid containing the plutonium was quantitatively removed, and a determination of the active element was made by reduction with zinc amalgam and potentiometric titration with ceric sulfate.[14] The two methods gave the following results:

Percent copper, electroanalysis,	81.61
Percent plutonium, potentiometric titration,	17.95
	99.56 percent.

With this amount of copper in a sample, it was found necessary to be rather careful in washing the amalgam, especially with the last washes of acetone. The mercury does not remain bright, as it does with about 20 mg of copper. A scum forms on the mercury surface during the water or acetone wash, and some of this material may be lost if care in washing is not taken. Nickel, and to a much greater extent cadmium, tend to react in this manner with amounts of metal not much greater than 20 mg on 10 g of mercury.

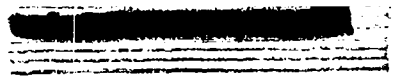
In making the analyses reported above, it was recognized that the deposition equipment was deficient in that it did not permit rinsing of the anode unit and



dilution of the electrolyte without discontinuing the electrolysis.

With metals no more active than nickel, cobalt, and copper, this is not a serious disadvantage, since 0.5 to 1.0 N sulfuric acid does not react appreciably with these metals when deposited on mercury. A few experiments with cadmium, however, have shown that this metal comes to the surface of the mercury more quickly, and some losses occur during the washing process. This separation on the surface of the mercury does not occur with bismuth, but the greater length of time for complete deposition of 20 mg of bismuth (60 minutes at 0.2 ampere) resulted in errors of 0.6 mg from other causes. Mercury was lost by volatilization and dispersion in the electrolyte; it was observed there later after the coagulation of the dispersed metal by partial evaporation of the electrolyte. Errors due to volatilization have been recognized and discussed by Bottger.[15]

Finally, to obtain an indication of the accuracy of the procedure introduced on p. 9, repeated analyses of known amounts of copper were made. The data given in Table IV show that slightly low results are obtained, and the average error was 0.08 mg or about



four parts per thousand. Similar accuracy can be expected with cobalt and nickel, since apparatus and technique cause more error than do differences in these metals.

Table IV

ACCURACY OF COPPER ANALYSIS

Wt. of Cu Taken	Wt. of Cu Found	Error
18.70 mg	18.64 mg	-0.06 mg
18.71	18.69	-0.02
18.75	18.60	-0.15
19.73	19.65	-0.08
19.66	19.53	-0.13
19.39	19.31	-0.08
20.12	20.10	-0.02
18.89	18.83	-0.06

[redacted]

CONCLUSIONS

Cobalt, nickel, and copper are quantitatively separated from plutonium by electrodeposition on a mercury cathode when the electrolyte is approximately 0.5 N H_2SO_4. Only submicrogram quantities of the radioactive element remain with the amalgam that is formed.

When the metals separated in this manner are determined by direct weighing, average errors up to 0.08 mg can be expected with samples containing 20 mg of the element that is being deposited on 3 to 10 g of mercury.

Under these conditions, as much as 100 to 200 mg of plutonium may be present in the sample.

Equipment for making these determinations is simple, and adequately prevents troublesome contamination by the plutonium.

The described analytical procedure has been tested by analysis of various binary plutonium alloys of cobalt, nickel, and copper.

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