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LOS ALAMOS SCIENTIFIC LABORATORY

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A MODIFIED CUPFERRON EXTRACTION AND SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF TRACE IMPURITY ELEMENTS IN PLUTONIUM

by

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ABSTRACT

Significant improvements were made on a previously reported spectrochemical procedure[1] for the determination of trace amounts of impurity elements in plutonium and are described. The procedure involves dissolving the metal sample, separation of plutonium by extraction of its cupferrate into an ether-chloroform phase, complete destruction of residual organic matter in the separated aqueous phase (containing the impurity elements) with nitric and perchloric acids, transfer of the fumed inorganic residue to copper electrodes, sparking with an air-interrupted high voltage source, and comparing the resultant impurity element spectra with that of standards carried through the identical procedure. The major modifications are perchloric acid destruction of organic residue and visual comparison of sample spectra with spectra of extracted standards. The method was developed primarily for the determination of those impurity elements, important for nuclear reasons, in high-purity plutonium metal ~~fabricated for weapon~~ use. The confidence error of the average of triplicate analyses of a single sample is ± 50 percent at the 95 percent significance level.

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INTRODUCTION

The analysis of plutonium metal for trace quantities of the high cross-section alpha or neutron-absorbing elements requires a method of extreme sensitivity with moderate accuracy and precision. The requirement of determining impurity element concentrations to a few parts per million and even to tenths of parts per million precludes most chemical methods. A spectrochemical method becomes a logical choice and has been used at this laboratory as well as at Hanford Works for the routine determination of the majority of the specification metal impurities in plutonium samples.

The cupferron extraction[1] and carrier-distillation[2] spectrochemical methods have been used for these analyses. Since the line-rich plutonium spectrum interferes with the spectra of impurity elements, any spectrochemical method of analysis must be based on the fact that it is necessary to eliminate the plutonium spectrum from that of the sample. In the cupferron procedure, plutonium cupferrate is extracted from an acid aqueous phase into an ether-chloroform phase. The separated aqueous phase is then spectroscopically analyzed for the impurity elements. In the carrier-distillation method, a carrier, such as gallium oxide, is intimately mixed by grinding with the plutonium oxide sample and this mixture arced in graphite electrodes. The lower volatilization temperature of the carrier prevents the thermal excitation of the more refractory compounds, in particular, plutonium oxide.

Both methods possess advantages and disadvantages. Experience at this laboratory has indicated that results from the two methods disagree. (A recent report[3] from the Hanford Works emphasizes this lack of agreement and presents evidence claiming the carrier-distillation method to be more accurate.)

Some of the advantages of the carrier-distillation method are potentially greater element coverage and less probability of contamination providing the sample ignition step is carried out in a furnace so constructed to prevent contamination of the sample from refractory insulation.

The cupferron extraction method can utilize the more stable copper spark excitation source developed by Nachtrieb and his co-workers[4,5,6]. This method of excitation excites all elements including the refractory forms not excited by the carrier-distillation technique. The plutonium extraction-copper spark technique also possesses the inherent advantage of a wide variation in sample size resulting in a greater range of impurity sensitivity than does the carrier-distillation technique.

Experience and preliminary investigations with the carrier-distillation method for analyses of uranium and plutonium oxides revealed great dependencies on several variables. One of these was matrix material density. Since spectroscopically pure plutonium, or its oxide, have not been available, standards in a uranium oxide matrix

have been used for plutonium analysis. The density difference between black uranium oxide and plutonium oxide is about 3.03 (8.41 compared to 11.44). This difference, reflected as a 30 percent difference in charge heights in the cratered graphite electrodes, was shown to have a very significant effect on the spectral line densities. Primarily because of these considerations, attention was centered on improvements that might be made in the previously-used cupferron procedure.

The exigencies during the early development of plutonium analysis prevented thorough investigation of the many variables involved in a spectrochemical extraction procedure. The variables considered most significant were (1) extraction of impurity elements by cupferron possibly due to co-extraction with plutonium cupferrate,(2) physical or mechanical loss of sample residue from electrodes during excitation, (3) contamination by reagents and apparatus,(4) transfer and fuming losses,and (5) inadequate plutonium removal thereby causing spectral line interference.

In the early development of the cupferron method essentially two approaches were followed to determine if significant amounts of the impurity elements were extracted into the organic phase and discarded along with the plutonium. These were (1) extraction of macro-amounts of impurity elements accompanied by gravimetric analysis of the two solvent phases and (2) spectroscopic estimation of the amounts remain-

ing in the aqueous phase following extraction of micro-quantities of these elements. Nachtrieb and Wexler[7] reported complete recoveries of fifty milligram quantities of sodium, lithium, and magnesium in extractions at pH 1.4. Cowan and associates[8] added ten milligrams of each of thirty elements and obtained recoveries of approximately 90 percent for the lower atomic number elements.

Earlier workers[9, 10, 11, 12, 13] studied the behavior of microgram quantities of certain elements during the extraction of plutonium cupferrate, relying upon spectrochemical analysis of the separated aqueous phase. Iron was often used as a "stand-in" for plutonium. In general, only slight losses from the aqueous phase were reported. In some cases the data were biased from severe contamination, while in others, inadequate data prevented drawing of firm conclusions. Nachtrieb[9] reported an average recovery of 87.3 percent (with a range of 49 to 200 percent) for thirteen elements based on photometered data of an internal standard and plate calibration procedure.

In other early attempts to establish losses in the extraction step, radioisotope tracer techniques were employed. Cowan and associates[8] and Hein and Voigt[14] applied this technique using Be^7. Cowan in his report, which did not include experimental data, found that 96 percent of the beryllium remained in the aqueous phase which was 7 percent by volume hydrochloric acid. Hein and Voigt found 98 percent of this element remaining in the aqueous phase after extracting macro quantities to which the tracer had previously been added.

It appeared logical that conclusions from some of these experiments could have been in error since there was no evidence that trace amounts of impurity elements would behave in the same manner as macro-amounts, especially in the presence of a large excess of plutonium. Neither did this early work make any attempt to study losses in other steps in the procedure. The over-all efficiency of the procedure was accordingly left in doubt.

The inherent danger of loss of material from the end-surface of an electrode during high voltage spark excitation was recognized by earlier investigators. Nachtrieb and Wexler[10] suggested that an ethereal, free-acid cupferron solution be used rather than the ammonium salt of this reagent since the formation of residual ammonium chloride, when transferred to electrodes, caused mechanical loss during the excitation period. Nachtrieb and associates[1] also recognized the possibility of mechanical loss and stated that residual organic matter should be substantially destroyed with 16 N nitric acid before transfer of the sample residue to the electrodes. Fred and co-workers[5] likewise recognized the seriousness of the problem and made various attempts to produce more satisfactory deposits by the addition of substances to the electrodes which dried in the form of a glass, such as phosphoric acid and various organic bases, but met with indifferent success. Better results were obtained for specific elements by electrodeposition on the copper electrodes.

In addition to the desirability of making certain improvements in the existing procedure, it was also considered advantageous to develop a procedure that would be more readily adaptable to routine use. The following characteristics were considered necessary or highly desirable.

1. A highly efficient one-step plutonium extraction procedure leaving not over fifty micrograms of plutonium in the aqueous or impurity phase.
2. Very low losses of impurity elements in the plutonium extraction process.
3. The apparatus should be simple, fabricated from materials that would introduce a minimum of contamination.
4. The procedure should be simple, adaptable to routine use and capable of being carried out with a minimum of exposure of personnel to plutonium.

Of the several solvents or complexing compounds that were reported[15, 16, 17, 18, 19] capable of removing plutonium to the required efficiency, only cupferron and thenoyltrifluoracetone seemed to meet all the requirements. ~~(Experiments in this laboratory revealed that thenoyltrifluoracetone failed to extract gallium. The presence of relatively significant quantities of gallium on the electrodes was found to cause large mechanical losses during excitation.) For this reason thenoyltrifluoracetone was eliminated as a useful plutonium-complexing agent in a procedure for the analysis of plutonium (fabri-~~

~~cated for weapon use.~~)

This report describes the work that led to the development of an improved analytical procedure for the determination of certain trace impurity elements in plutonium. It is based on separation of plutonium by extraction of its cupferrate into an ether-chloroform phase, complete destruction of residual organic matter in the impurity element-containing aqueous phase with nitric and perchloric acid, transfer of the fumed residue to copper electrodes, sparking with an air-interrupted spark, and comparing the resultant impurity spectra with that of standards carried through the identical procedure.

APPARATUS AND REAGENTS

A. Apparatus

1. Chemical Process Dry Box.

A stainless steel dry box, 90 inches long and partitioned into two sections, 60 inches and 30 inches, respectively, was used. The larger section was equipped with two complete sets of apparatus. The smaller section was used for dissolving samples and recovering spent solutions. Figure 1 is an exterior view of the dry box and Figs. 2 and 3 are views of the larger and small sections with apparatus in place.

2. Volumetric Glassware.

a. Volumetric flasks, quartz, 4 ml, regular shape. (Figure 3).

b. Extraction vials, quartz, 1 ml, test tube shape, 9/15 T. (Figure 5).

c. Micropipettes, quartz, 25, 50, 100, 200, 500 microliters. (Figure 8).

d. Transfer pipette, quartz, 1 ml. (Figure 3).

e. Syringes, glass, with tygon tubing fittings for micropipettes, (Figures 3, 8).

f. Graduated cylinder, quartz, 25 ml. (Figure 2, on shelf).

3. Platinum Ware.

a. Crucibles, 1.3 ml, bottoms pressed to an 8 degree taper. (Figure 6).

b. Drying rack for crucibles. (Figure 6).

4. Lucite Ware.

a. Holder for 4 ml volumetric flasks, 10 holes. (Figure 3).

b. Holder for platinum crucibles with individual covers. (Figure 6).

c. Holder for 1 ml extraction vials, 36 holes. (Figure 5).

d. Shaker box for 1 ml extraction vials and holder. Used to uniformly and simultaneously shake 36 extractions. (Figure 5).

5. Drying Chambers and Heaters.

a. Heaters, with stainless steel reflectors and nichrome elements. (Figures 4, 6).

b. Pyrex drying chamber made with a ground glass base plate. The chamber was connected to an all-glass water aspirator which was used to remove water and acid vapors. (Figure 7).

6. Electrode Drying Apparatus.

a. Electric hot plate, 4 inches in diameter, variac controlled. (Figure 8).

b. Electrode holder made of a copper disc, 4 inches in diameter, 1 inch thick, twelve holes drilled for electrodes, and with a pyrex cylinder and cover plate. (Figure 8).

c. Wood blocks, 12 holes drilled for electrodes and plastic covers. Used to hold electrodes after machining and before

sparking.

7. Quartz Stills.

   a. Normal pressure, 18-inch quartz-packed reflux column. (Figure 9).

   b. Vacuum, 7-inch quartz-packed reflux column. Used for purification of perchloric acid. (Figure 10).

8. Spectrograph and Accessories.

   a. Jarrell-Ash, stigmatic, 21-foot, grating spectrograph.

   b. National Spectrographic Laboratories "Spec-Power" source, Model No. 1212, 5KVa air-interrupted spark.

   c. Dry box sparking chamber with quartz window on optic axis.

   d. Bausch and Lomb arc stand with laboratory installed spring clamp electrode holders. (Figure 11).

   e. Condensing lens, quartz, which focused spark on spectrograph slit. (Figure 11).

   f. Remote control box, foot operated which controlled plate racking, electrode alignment light, and excitation source.

B. Reagents

All reagents were stored in quartz. Cupferron was kept refrigerated in an atmosphere of ammonia maintained in a desiccator partially filled with ammonium carbonate[20].

1. Water and Acids.

Water, hydrochloric acid, and nitric acid were distilled at atmospheric pressure (590 mm Hg) in quartz stills (Fig. 9). Perchloric acid (70-72 percent) was distilled in a vacuum quartz still at an absolute pressure of 50-70 mm Hg maintained by a water aspirator. (Figure 10).

2. Organic Solvents.

Reagent grade chloroform and diethyl ether were usually satisfactory. They were distilled when tests showed contamination with impurity elements.

3. Cupferron.

Purified by dissolving 25 gm technical grade ammonium salt in 250 ml water in a separatory funnel and treating as follows: The free hydroxylamine was precipitated by addition of 50 ml quartz-distilled hydrochloric acid and then extracted into 100 ml diethyl ether at low temperature to prevent boiling of the ether and air oxidation of cupferron. The aqueous phase containing the metal impurities was discarded and the free hydroxylamine re-extracted into 100 ml of a saturated ammonia solution. Pure ammonia was most easily prepared by bubbling ammonia gas from commercial cylinders through quartz-distilled water in a quartz tower. The ammonium salt of cupferron was then precipitated with excess acetone and collected on an 18.5 cm Whatman 41 H grade filter paper

in a Buchner funnel.

C. Preparation of Copper Electrodes[5, 9].

One and one-half inch lengths of one-quarter inch electrolytic copper rod were washed in dilute nitric acid and rinsed in distilled water. After drying, the rods were machined with a smooth polishing cut along three-quarters inch of the length and across the end. The electrodes were placed in the wood blocks and covered with the plastic covers until used for analyses. Freshly machined electrodes should be used since copper oxide formation increases background density. Electrodes prepared in this manner were found to be spectroscopically free from the elements involved in this work.

EXPERIMENTAL RESULTS AND DISCUSSION

I. Extraction Studies of Certain Elements by Radiotracer Methods

The radioisotopes listed in Table I[21, 22, 23] were used to establish losses of certain elements during the plutonium-separation (extraction) process. The "Recommended Procedure" was followed to determine these losses under identical conditions of sample analysis. This study was limited by the number of suitable isotopes available. (~~Gallium was included because many of the samples to which the method applies contain significant quantities of this element.~~)

Two levels in the usual range of impurity concentration were chosen for

investigation for all the isotopes except beryllium. An insufficient quantity of beryllium 7 prevented investigation with this isotope at more than one concentration level..

Table I

Radioisotopes Used for Cupferron Extraction Studies

Isotope	Half-Life	Decay Form and MEV Energy		Chemical State
Sodium 22	3.0 years	B^+	0.575	Carrier Free (Oak Ridge)
		γ	1.3	
Beryllium 7	52.9 days	K(γ)	0.748	Carrier Free (Oak Ridge)
Calcium 45	152 days	B^-	0.26	Carrier Free (Oak Ridge)
Lanthanum 140	40 hours	B^-	1.4 0.90 2.12	Matrix of La 139 (Los Alamos)
		γ	5 decays ranging from 0.335 to 2.40	
Gallium 72	14.3 hours	B^-	7 decays ranging from 0.56 to 3.17	Solid $Ga(NO_3)_3$ (Oak Ridge)
		γ	7 decays ranging from 0.84 to 1.57	

The carrier-free isotopes of sodium, beryllium, and calcium were added in desired millicurie quantities along with the concentration levels of the normal element. The isotopes of lanthanum 140 ~~and gallium~~, already in matrices of the normal element, were added in desired microgram levels which fortunately gave counting data in a statistically sound range.

Quadruplicate extractions under four different conditions were made

for each isotope at each concentration level. These conditions were, blanks (no plutonium, no isotope), plutonium only, isotope only, and plutonium with isotope. Thus, by combinations of counting data, losses in the extraction process were calculated for the five elements in the absence and presence of plutonium. Statistics recommended by Friedlander and Kennedy[24] were applied.

The counting equipment (Fig. 12) consisted of an amplifying circuit and counter manufactured by the laboratory's instrument section (CMR-7), an end window Geiger tube (amperex 100C) mounted in a lead counting chamber, stainless steel sample dishes, and Lucite holders for the dishes.

After completion of the extraction, aliquots of the aqueous phase were transferred to stainless steel dishes, evaporated to dryness, and counted. A double thickness of cellophane was placed between the dish and Geiger tube during counting to absorb the interfering alpha particles from plutonium. Since the cellophane shield affected beta and gamma countings, it was used in counting all samples. Time corrections ~~were~~ was applied for the effect of the short half-~~lives~~ life of lanthanum 140 ~~and gallium 72.~~ Table II is a summary of the results.

Table II

Radioisotope Tracer Studies of Some Elements Remaining in the Aqueous Phase from the Cupferron Extraction

Element	ppm (Based on 5 mg Plutonium)	Recovery in Percent (Average and Standard Deviation) Element Only	Element + Plutonium
Sodium	10	95.3 ± 4.3	101.5 ± 3.0
	100	102.0 ± 4.2	100.8 ± 4.7
Beryllium	5	95.2 ± 2.9	94.2 ± 4.4
Calcium	80	89.0 ± 3.6	89.0 ± 4.1
	320	97.3 ± 4.7	102.7 ± 5.8
Lanthanum	420	95.1 ± 6.3	98.8 ± 3.5
	480	97.8 ± 6.3	94.0 ± 3.8
Gallium	60	0.15 ± 0.60	- 6.4 ± 6.4
	300	0.90 ± 0.25	0.01 ± 0.07

These data indicated that (1) gallium was completely extracted as the cupferrate into the organic phase, (2) the other elements essentially remained in the aqueous phase, and (3) plutonium had no effect on their behavior.

Additional counting data indicated that 99.5 percent of the plutonium was removed as the cupferrate into the organic phase and that the recovery of sodium 22 carried completely through the "Recommended Procedure" was 85 percent.

II. Mechanical Loss of Impurity Residue from Electrodes During Excitation

Although it was suspected that the destruction of organic residue by nitric acid was not complete in the previous cupferron procedure[1], no evidence of the extent of the mechanical losses caused by the presence of organic material during excitation was available. It was also recognized that such losses, if they existed, would yield low results if the spectra from an analysis were compared to the spectra obtained from standards placed directly on electrodes using dilute hydrochloric acid as a solvent and therefore under conditions in which no organic residue was present.

To obtain evidence of any relationship between the presence of organic material and possible mechanical losses from the electrodes during the sparking process, the following experiment was carried out. Extractions were made of lanthanum-free plutonium and of blanks (reagents without plutonium). The aqueous phases were separated, dried, fumed with 16 N nitric acid and the resultant residues transferred and evaporated on electrodes. Known quantities of lanthanum, as chloride, were then added and evaporated and the material sparked. The resulting spectra were compared to spectra obtained from lanthanum standards evaporated directly on electrodes as lanthanum chloride.

Quadruplicate analyses were made by each of two analysts for each series in Table III. In each case plate calibration and background correction

were taken into consideration in calculating the data from the photometered line densities.

Table III

Losses of Lanthanum During Excitation Attributed Directly to Organic Residue Present on Electrodes

Micrograms La Added	Percent Recovery and Standard Deviation Analyst A	Analyst B
0.1 (No plutonium)	31 ± 17	27 ± 13
0.1 (5 mg Plutonium in Extraction)	50 ± 14	12 ± 13
0.4 (No plutonium)	25 ± 13	15 ± 14
0.4 (5 mg Plutonium in Extractions)	43 ± 12	5 ± 5

The recoveries, ranging from 5 to 50 percent, were poor and erratic and indicated substantial losses during the excitation period. These losses were attributed directly to the organic material present on the electrodes. These erratic recoveries made it obvious that results based on comparison of sample spectra to either spectra of standards evaporated directly on electrodes or to spectra of standards treated in an identical manner as samples might be low from two to twenty fold.

Various attempts were made to reduce mechanical loss during excitation. These included such techniques as (1) coating the electrodes with a thin layer of **Lucite**, (2) substituting graphite for copper electrodes, with and without **Lucite** coating, (3) direct current excitation in shallow crater graphite electrodes with gallium oxide as a carrier and, finally, (4) use of perchloric acid to completely destroy organic material. None of the techniques tried except the latter was considered satisfactory.

III. Effects of Perchloric Acid Destruction of Organic Residue on the Recovery of the Impurity Elements

Preliminary experiments of fuming with various volumes of quartz-distilled 70 percent perchloric acid, either with or subsequent to fuming with nitric acid, gave promising results. Further work showed that fuming with 100 microliters of perchloric acid, subsequent to fuming with nitric acid, as described under "Recommended Procedure." was the best method for complete destruction of organic residue. The data in Table IV represent the recovery of eight standards in triplicate carried through the "Recommended Procedure," with the exception that only water was used to transfer the perchloric acid-fumed residue to the electrodes. Attempted transfers with quartz-distilled hydrochloric acid were unsuccessful due to the corrosion of the copper electrodes from appreciable amounts of formed perchloric acid. The recoveries were based on photometered density data comparing the extracted standards to the same standards evaporated as chlorides directly on electrodes.

Table IV

Effect of Perchloric Acid Fuming on the Recovery of Certain Elements

Element	Range in ppm (Based on 5 mg Plutonium)	Percent Recovery and Standard Deviation Plutonium Absent	Plutonium Present
Li	0.2-4.0	92 ± 17	85 ± 11
Na	2.5-100	96 ± 13	98 ± 19
K	50-100	102 ± 7	119 ± 19
Be	0.2-4.0	70 ± 13	79 ± 13
Mg	2.5-100	88 ± 20	84 ± 21
Ca	2.5-15	92 ± 21	92 ± 16
Al	5.0-100	48 ± 7	41 ± 23
La	10-400	51 ± 12	43 ± 18

These data indicated that (1) treatment with perchloric acid gave greatly improved reproducibility, (2) significantly low recoveries were obtained for beryllium, aluminum, and lanthanum, (3) a tendency for higher than theoretical 85 percent recovery (radioisotope tracer data) existed for all elements except the above three, and (4) plutonium in the extractions had no effect on the impurity-element recoveries.

Further investigations revealed that the perchlorate ion enhanced the spectral sensitivity of some elements, particularly the alkali metals, and at the same time decreased the "sensitivity" (or actual recovery on transfer to electrodes) of beryllium, aluminum, and lanthanum. The decreased sensitivity of these three elements was thought to be due possibly to formation of their water-insoluble oxides during the perchloric acid fuming.

Since a procedure had now been established with adequate reproducibility,

it became possible to develop a routine method in which sample spectra would be compared to standards treated in an identical manner, except that plutonium need not be included in the extractions. This technique would remove the bias associated with each element from the perchloric acid fuming as well as the 15 percent overall process loss. However, the sensitivity limits would be lower than desired for aluminum and lanthanum.

Obviously an increase in the sensitivity limits for these elements would be obtained if an acid, such as hydrochloric, which would dissolve the water-insoluble oxides, were used to transfer the fumed residue to the electrodes. Since previous experiments showed that constant boiling hydrochloric acid (6.24 N at Los Alamos altitude) reacted with the perchloric acid-fumed residue to badly corrode copper electrodes, a series of experiments were planned and executed to find the optimum solvent system for the transfer. These statistically controlled and analyzed experiments included such variables and their interactions as volume and normality of hydrochloric acid solvent, use of water and/or hydrochloric acid, order of their use, and personnel factors. For these studies, a prepared standard was divided into 64 aliquots, carried through the extraction and perchloric acid fuming as described under "Recommended Procedure," and the resulting residues treated and transferred to the electrodes. The data in Table V were calculated from photometrically measured line densities. Elements included were beryllium, lithium, magnesium, aluminum, and lanthanum.

Table V

Summary of Analyses of Variance for Recovery of Certain Elements as a Function of Composition of Residue Transfer Solvent

Element	Order of	Significance of Solvent Variable		
		Normality	Volume	Interaction of Volume and Normality
Lithium	None	99 percent 0.5 N, low recovery. 1.0-6.0 N, random.	None	None
Beryllium	None	None	None	99 percent 100 microliters of 3.0 or 6.0 N, low recovery. 50 microliters of 1.0 N, high recovery.
Magnesium	None	None	None	95 percent 100 microliters of 3.0 or 6.0 N, low recovery. 50 microliters of 1.0 N, high recovery.
Aluminum	99 percent water, then acid, best	None	None	95 percent 100 microliters of 3.0 or 6.0 N, low recovery. 50 microliters of 1.0 N, high recovery.
Lanthanum	None	None	None	99 percent 100 microliters of 3.0 or 6.0 N, low recovery. 50 microliters of 1.0 N, high recovery.

A statistical analysis of variance produced the following conclusions:

1. There was an inter-relationship between volume and normality for maximum recovery of all elements except lithium.
2. The best order of using transfer solvents for recovery of aluminum was water followed by hydrochloric acid.

3. The highest, as well as the most consistent, recoveries were obtained when the transfers of residues from crucibles to electrodes were made by first using 100 microliters of water, followed with 50 microliters of 1 N hydrochloric acid.
4. No difference was indicated between analysts or different sets of apparatus.

IV. Studies of Other Variables

A. Acid Normality of Extractions.

Since the radioisotope tracer studies had shown that gallium was completely extracted as the cupferrate from an aqueous solution within the acid range of 0.65 to 0.85 N, the behavior of aluminum, a "specification" element and a member of the same periodic subgroup, was investigated. The "Recommended Procedure" gave sufficient accuracy and precision to determine the effect of hydrogen ion concentration on the aluminum cupferrate equilibrium.

A series of extractions of sub-microgram quantities of aluminum were made following the "Recommended Procedure" except to vary the free acid normality over the range 0.1 to 1.0 N.

This study revealed that the aluminum cupferrate equilibrium was a function of hydrogen ion concentration and that increased acidity gave increased recoveries of aluminum in the aqueous phase. Since this acid range was also that in which the plutonium cupferrate

equilibrium was likewise affected (but to a lesser degree), a normality of 0.82 ± .02 was chosen for the "Recommended Procedure." This level gave essentially complete recovery of aluminum with 99.5 percent removal of plutonium.

B. Spark Circuit Constants and Exposure Time.

The recommended conditions[1] for excitation had been the use of a Dietert Spark Unit (No. 2025) set at 2 KVa input (320 microhenries inductance and 21 millimicrofarads capacitance) with a 2.0 mm gap and 50 second exposure. Nachtrieb[25] expressed the opinion that the excitation conditions are not highly critical but should be maintained as constant as possible once selected.

Since the "Spec-Power" source is designed with wide limits and separate settings for the various circuit parameters, a series of factorial experiments were designed to establish optimum spark conditions. The variables were power input, auxiliary air gap, secondary inductance, secondary capacitance, analytical gap, and exposure time.

These studies, though not complete at this writing, indicated that secondary inductance and secondary capacitance were important variables and also that exposure time was interrelated with power input in a significant manner. The other variables had unimportant effects on the spectral line densities. A very satisfactory combination of parameters was found to be

2.8 KVa input, 3.5 mm auxiliary air gap, 100 microhenries inductance, 15 millimicrofarads capacitance, 2.5 mm analytical gap, and a 30 second exposure.

C. Choice of Photographic Plates.

Table VI

Principal Lines of Some Elements

Element	Wavelength 1st Order	2nd Order
Li	6707.85	
Na	5889.95	
K	7664.91	
Be	3130.42	6260.84
Mg	2795.53	5591.06
Ca	3933.67	7867.34
Al	3961.53	7923.06
La	3949.10	7898.20

Consideration of the wavelengths of the principal lines of the elements listed in Table VI led to the conclusion that the region 5500-8000A would include the first order alkali metal lines, as well as the second order lines of the other five elements, and could conveniently be used to photograph the spectra of all of the elements. The Jaco-21 foot spectrograph photographs about 2700 angstroms on twenty inches of plate, thereby adequately covering this region.

Adequate emulsion sensitivity and contrast was obtained[26] by using the 103a-F emulsion from 5500 to 6850A, the ammonium carbon-

ate sensitized I-N emulsion at the potassium line region, and the 103 or 103a-O emulsion from about 7800 to 8100A. A jig was made which enabled the cutting of 2 x 4-inch pieces of the O and N emulsions from 4 x 10-inch plates.

V. Quality Control

In order to establish the accuracy and precision of the "Recommended Procedure," a series of twenty unknowns prepared from mixtures of standards were analyzed by two analysts. Two known standards, one low and one high concentration level, were included in each of the two runs. Arithmetical factors were computed by comparing these two standards to the standard plate which contained spectra of twelve standards carried in triplicate through the "Recommended Procedure."

The spectra of these synthetic unknowns were read independently by four analysts. A 21X comparator was used that placed the spectra from the two plates into juxtaposition. Each of the triplicates was not read as such, rather an average of the three was recorded. These averages were corrected for the difference between plates based on the comparison of the two known standards.

The computed average of the four analysts and the calculated confidence error at the 95 percent significance level of the visually estimated average of triplicates are included in Table VII. This confidence error signifies the maximum limits within which 95 percent of the re-

ported estimates will lie.

Table VII

Accuracy and Precision of the "Recommended Method"

Element	Concentration Range (ppm) (Based on a 5 mg Plutonium Sample)	Average Recovery in Percent	95 Percent Confidence Error For a Single Sample
Li	0.2-4.0	110	34
Na	5.0-250	119	54
K	50-500	125	54
Be	0.2-4.0	108	42
Mg	5.0-250	106	60
Ca	5.0-250	113	50
Al	5.0-500	90	34
La	10-1000	117	40

The average recoveries were generally slightly greater than 100 percent. This was caused by differences between plates not completely compensated by the arithmetical factors. The factor should be near unity to obtain maximum accuracy. For this reason it is strongly recommended that the "Recommended Procedure" be adhered to by controlling such variables as the machining of electrodes, excitation conditions, and developing process.

The elements sodium, magnesium, and calcium had poor precision due to random contamination. The contamination levels were 3 ppm sodium, 2 ppm magnesium, and 2 ppm calcium. The use of Pyrex instead of quartz approximately doubles these levels and results in greater error. Potassium showed poor precision due to the unreproducibility of the

sensitized emulsion.

RECOMMENDED PROCEDURE

Caution

Any work involving the handling of plutonium-containing materials should be done under approved conditions and in laboratories designed for the adequate protection of the worker. Rules recommended by the Health Group for the safe handling of such materials should be rigidly followed.

All reagents are those described under "Apparatus and Reagents" and are used undiluted unless otherwise specified. A 200 mg sample is dissolved (although only 5 mg aliquots are analyzed) to reduce sampling error caused by segregation of impurity elements. The equipment has been designed to analyze 10 samples and 2 standards in triplicate at one time.

1. Sample Dissolution.

Dissolve 200 ± 10 mg of the plutonium metal sample in a 4 ml quartz volumetric flask by adding three 200 microliter portions of HCl. (Not less than one minute intervals.) Add an additional 1 ml HCl and gently heat if any undissolved particles remain. Make to volume with water. In general, the formation of insoluble plutonium oxide may be prevented by placing the first addition of 200 microliters of acid in the flask before adding the sample.

2. Preparation of Samples for Extraction.

Transfer three 100 microliter aliquots of dissolved sample, each

containing 5 ± 0.25 mg plutonium, to 1 ml extraction vials and add 100 microliters HCl to each. Make to volume with water.

3. Preparation of Standards for Extraction.

Add one lower and one of the higher concentration level standards in triplicate to 1 ml extraction vials and add 130 microliters HCl to each. Make to volume with water. (The standards should have been prepared by dissolving the metals or compounds in minimum HCl and diluting to volume with water.) A greater volume of acid is added to the standard extractions to make their normality the same as those of the samples.

4. Extraction of Samples and Standards.

Dissolve 2 gm of purified cupferron in 18 ml water in the graduated cylinder. Add 4 ml ether and extract the cupferron as the free hydroxylamine into the ether phase by adding 2.5 ml HCl. Add 100 microliter aliquots of the ether phase to each extraction vial and cause an intimate mixing of the two phases by agitating vigorously for 5 minutes.

Add 100 microliters of chloroform to each of 3 extractions at a time. (Do not add chloroform to all the extractions at one time as excessive air oxidation of the extractions will occur.) Gently agitate the extractions and transfer the aqueous phases to the platinum crucibles.

5. Treatment of Aqueous Phase.

Evaporate slowly to dryness (about 1 hour) in the drying chamber. Add 100 microliters HNO_3 and evaporate slowly to dryness (about 1/2-hour). Add 100 microliters $HClO_4$ and again evaporate slowly to dryness (about 1/2-hour). Remove the last traces of perchloric acid by heating to about 116° C for 10 minutes.

6. Transfer of Inorganic Residue to Electrodes.

Add 100 microliters water to each crucible. Use a different micropipette for each sample (3 extractions). To aid solubility, loosen the inorganic residue by thoroughly scraping the inside of the crucible with the tip of the pipette. Transfer the water addition in nearly equal portions to a pair of copper electrodes placed in the heated copper drying block. Add 50 microliters 1N HCl and again firmly and thoroughly scrape the crucible with the tip of the pipette. Transfer this acid addition to the previously coated pair of electrodes.

7. Excitation.

Transfer the electrodes to the wood blocks, cover with the plastic covers, and transport to the sparking dry box. Excite under the conditions specified in Section IV-B, Experimental Results and Discussion.

8. Development of Plates.

Develop in D-19 Eastman Kodak Developer at 18.0 ± 0.1° C for 5

minutes. Use an acetic acid short stop and fix in Eastman Kodak Acid Fixer.

9. Reading of Plates.

Use any comparator capable of juxtapositioning spectra from two plates. Visually compare the densities of triplicate spectra of 10 samples and 2 standards against standard plates. The standard plates should contain triplicate spectra of 12 standards which have been carried through this "Recommended Procedure." Estimate the average density of the triplicate spectra of the samples in terms of ppm of the impurity elements on the standard plate. Correct these estimations with factors computed from comparison of the 2 standards on the sample plate and the equivalent standards on the standard plate. Some typical spectra obtained by this recommended procedure are shown in Figs. 13 and 14.

10. Recovery of Plutonium.

Transfer the unused portion of the dissolved sample by vacuum to a residue bottle for future recovery. Transfer the plutonium cupferrate by vacuum to a separate residue bottle with the aid of a suitable solvent such as trichloroethylene. Take the necessary precautions to prevent plutonium from being lost or passing into the laboratory vacuum system.

11. Cleaning of Apparatus.

Soak and rinse all quartz and platinum ware in two successive

portions of warm commercial grade nitric acid. Save the spent nitric acid for recovery of plutonium. Thoroughly rinse each piece with distilled water, making a final rinse with quartz-distilled water immediately before use. Do not dry the rinsed apparatus with cloth or paper as this will introduce impurity contamination.

12. Time Estimate of Analyses.

Two trained analysts can completely process 70 samples during a 40 hour week. This is a rate of 7 impurity elements per hour based on analysis of 8 impurity elements per sample.

CONCLUSIONS

An improved spectrochemical procedure for the determination of trace amounts of impurity elements in plutonium has been developed. The improvements made in the previously-existing cupferron extraction procedure[1] were the use of perchloric acid to destroy organic residue and visual comparison of impurity element spectra from samples with spectra of standards carried through the identical procedure.

Radiotracer experiments applied to cupferron extractions in the hydrochloric acid normality range of 0.65 to 0.85 demonstrated that gallium was completely extracted, while sodium, beryllium, calcium, and lanthanum remained in the aqueous phase. Additional tracer experiments indicated that the extraction process removed 99.5 percent of the plutonium and that the recovery of impurity elements in the recommended

procedure does not exceed 85 percent.

An investigation of possible loss of residue from electrodes during excitation was made. It was found that nitric acid fuming of the aqueous phase containing the impurity elements did not adequately destroy the organic residue, since large and variable losses caused by purely mechanical loss still prevailed. Of the several attempted modifications to correct this error, the use of perchloric acid fuming was found to be most satisfactory.

A modified method incorporating perchloric acid fuming was developed. It was found necessary to compare spectra from samples with spectra of standards carried through identical procedures due to the effect of perchloric acid fuming on the spectral densities of the impurity elements as well as compensating for overall process losses. Perchloric acid fuming enhanced the spectral densities of certain elements, particularly the alkali elements, and decreased the spectral densities of certain other elements by forming water-insoluble oxides. Factorial experiments were made to find the best combination of solvents for transfer of the fumed residue from the crucibles to electrodes. An optimum order and composition was 100 microliters water followed by 50 microliters 1 N hydrochloric acid.

The aluminum cupferrate equilibrium was found to be a function of hydrogen ion concentration in the normality range of 0.1 to 1.0.

A normality of 0.82 ± .02 was chosen for the extractions in the "Recommended Procedure," as this level gave essentially complete recovery of aluminum with 99.5 percent removal of plutonium.

Limited experiments were conducted on circuit parameters and exposure time for the copper spark excitation. A very satisfactory combination was 2.8 KVa input, 3.5 mm auxiliary air gap, 100 microhenries inductance, 15 millimicrofarads capacitance, 2.5 mm analytical gap, and a 30-second exposure.

The use of a combination of 103a-F, 103a-O or 103-O, and sensitized 1 N emulsions was found capable of adequately photographing the spectral lines of several elements, including the alkali elements, in one exposure. Their placement was determined for the 20-inch casette of the Jarrell-Ash stigmatic 21-foot grating spectrograph.

A "Recommended Procedure" has been described which has a confidence error of ± 50 percent at the 95 percent significance level for the average of triplicate analyses of a single sample.

Figure 1

Exterior View of Chemical Process Dry Box
with Normal Number of Operating Personnel

Figure 2

Interior View of Larger Section of Dry
Box Showing a Complete Set of Apparatus

Figure 3

Interior View of Smaller Section of Dry Box Showing Sample Dissolving and Sample Recovery Apparatus

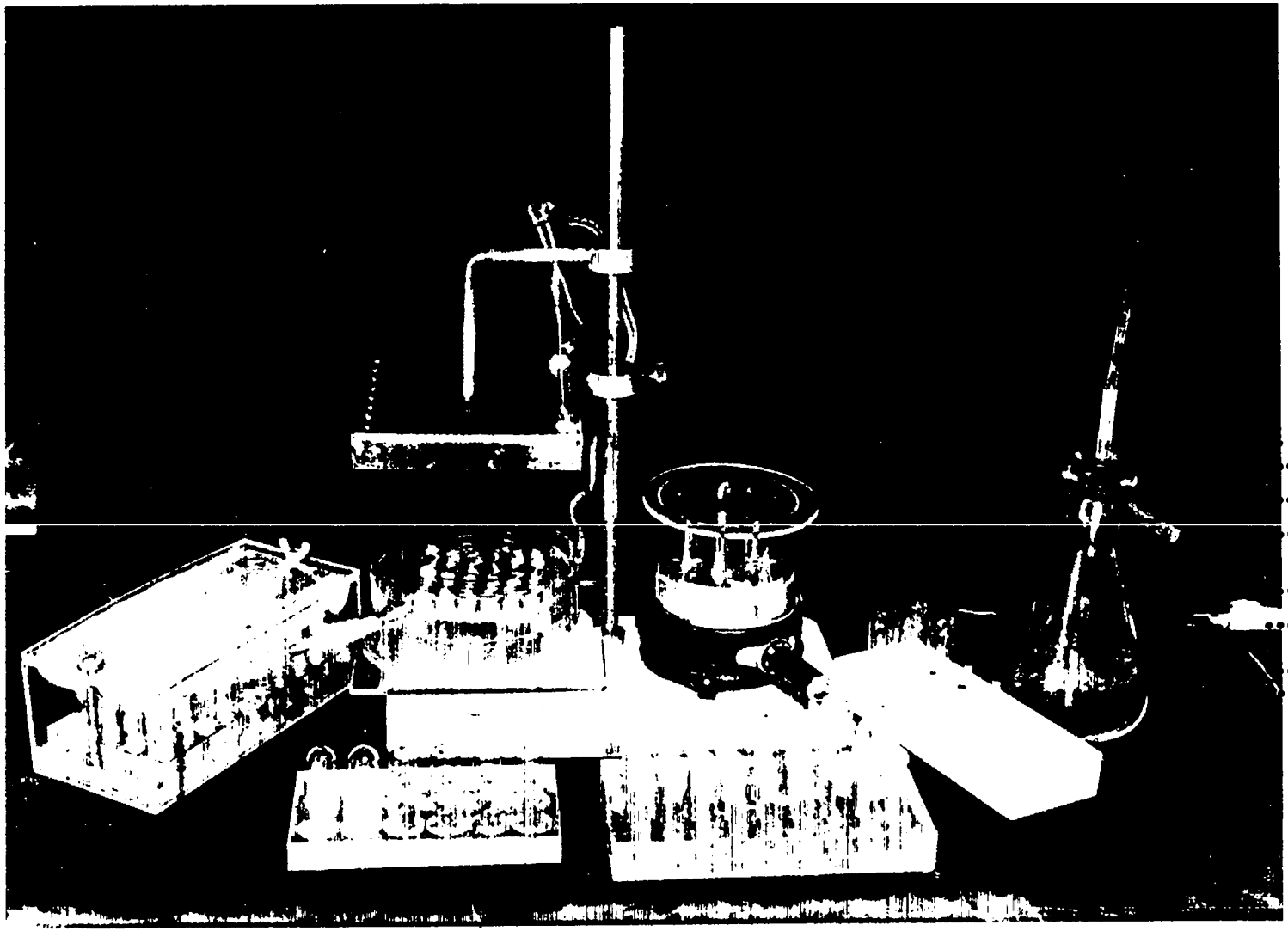

Figure 4

Apparatus for the Extraction Process
and for Residue Transfer to Electrodes

Figure 5

Volumetric Glassware, Lucite
Holders, and Shaker Box

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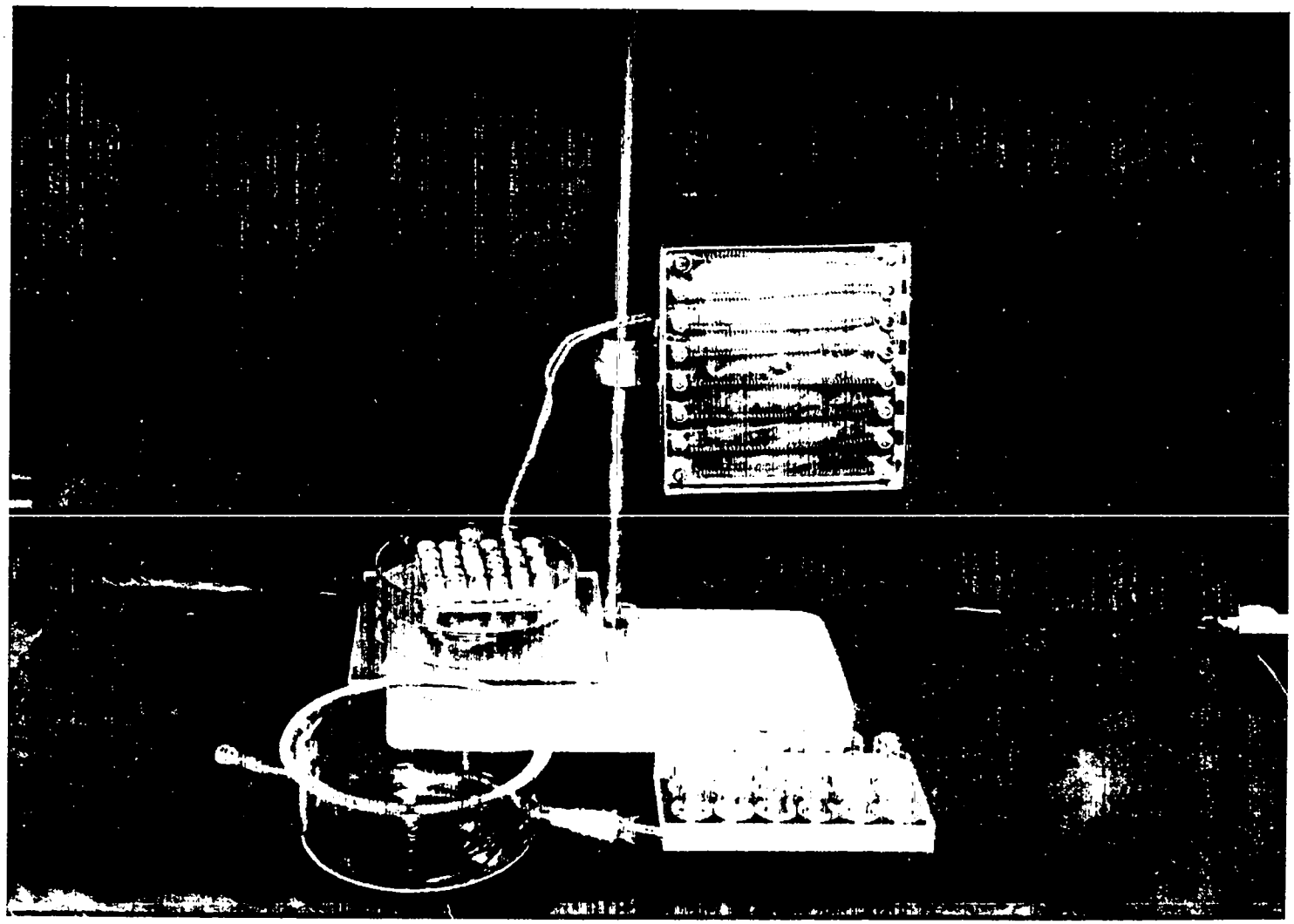

Figure 6

Drying Chamber, Platinum Crucible Holder, with Crucibles, Lucite Crucible Holder with Covers, and Stainless Steel Nichrome Wound Heater

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Figure 7

Detail of Drying Chamber and
Fittings to Glass Water Aspirator

Figure 8

Apparatus for Coating, Drying,
and Transfer of Copper Electrodes

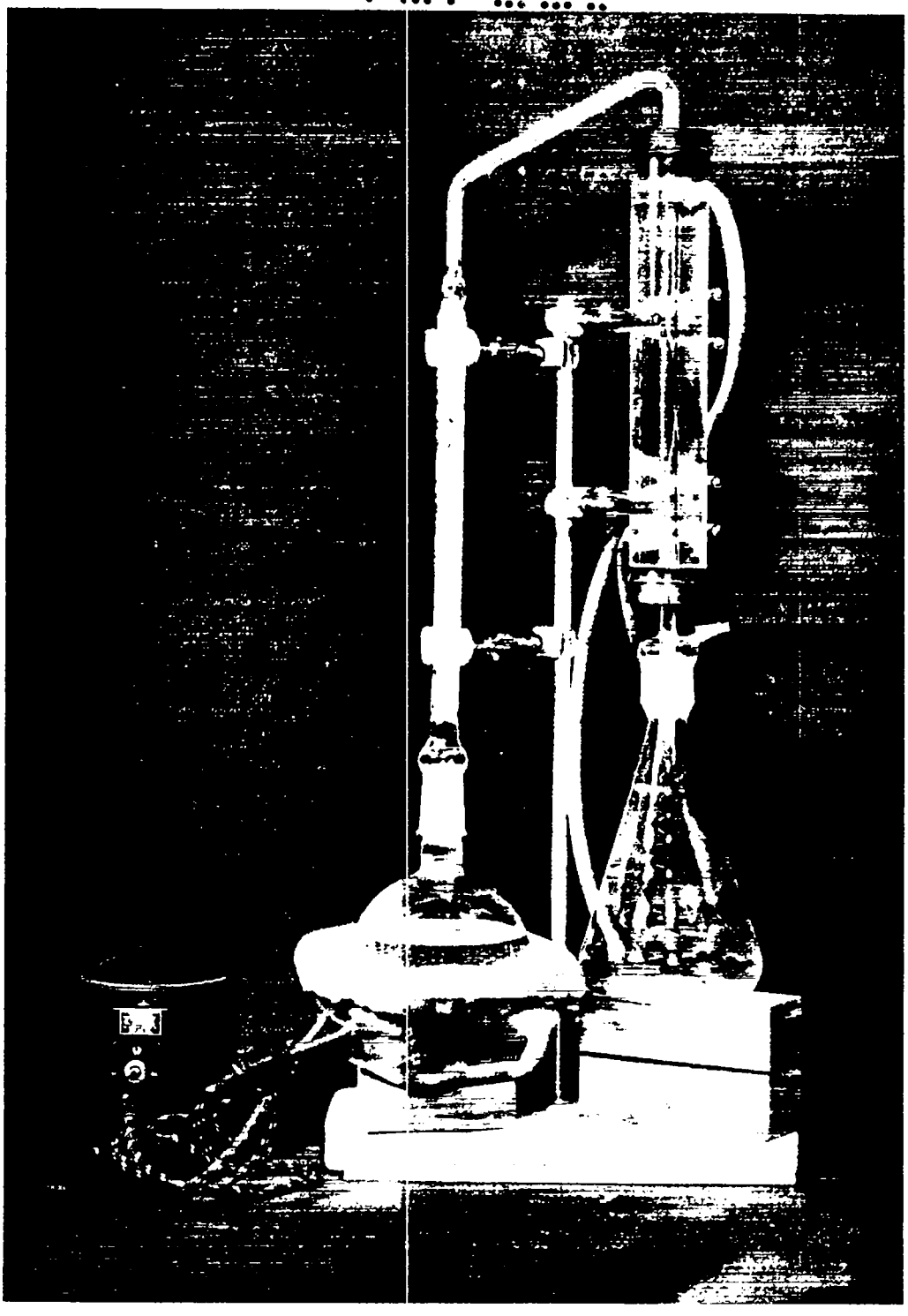

Figure 9

Normal Pressure Quartz Still

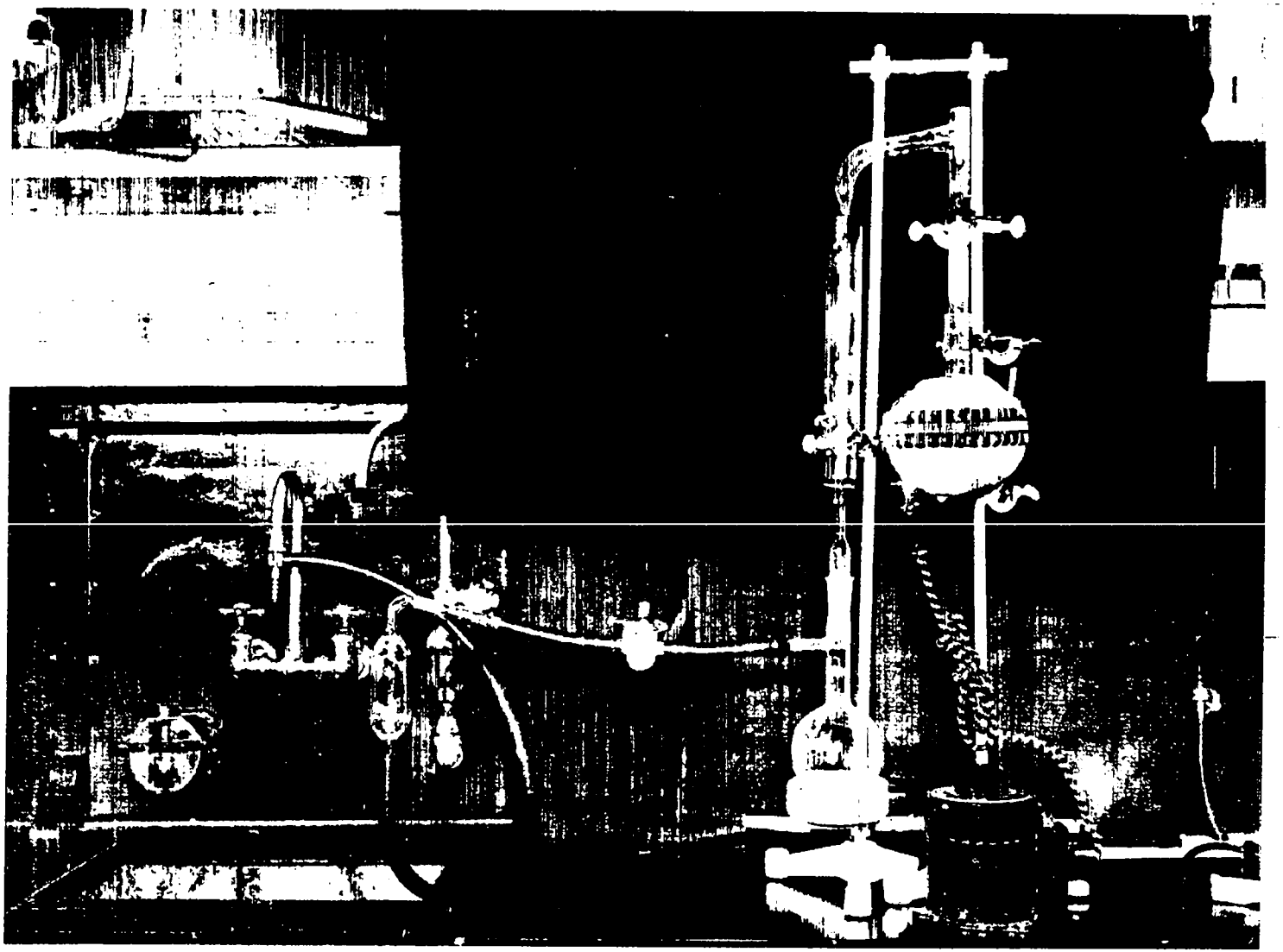

Figure 10

Vacuum Quartz Still for Perchloric Acid
Purification Connected to Water Aspirator

Figure 11

Interior View
of Sparking Dry Box

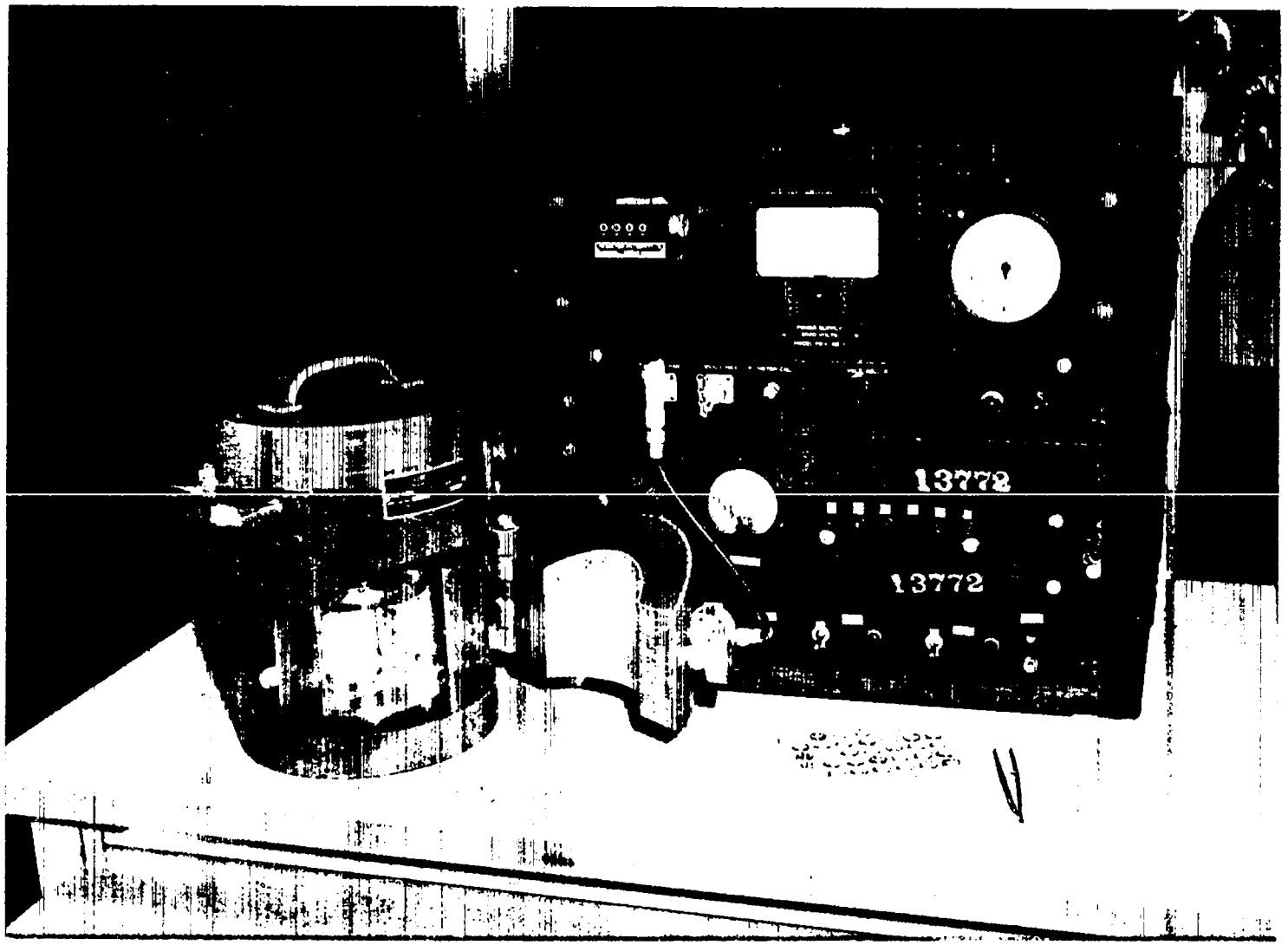

Figure 12
Tracer Chamber, Counter,
Crucibles, and Lucite Mount

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Figure 13
Plates Showing Magnesium Spectra

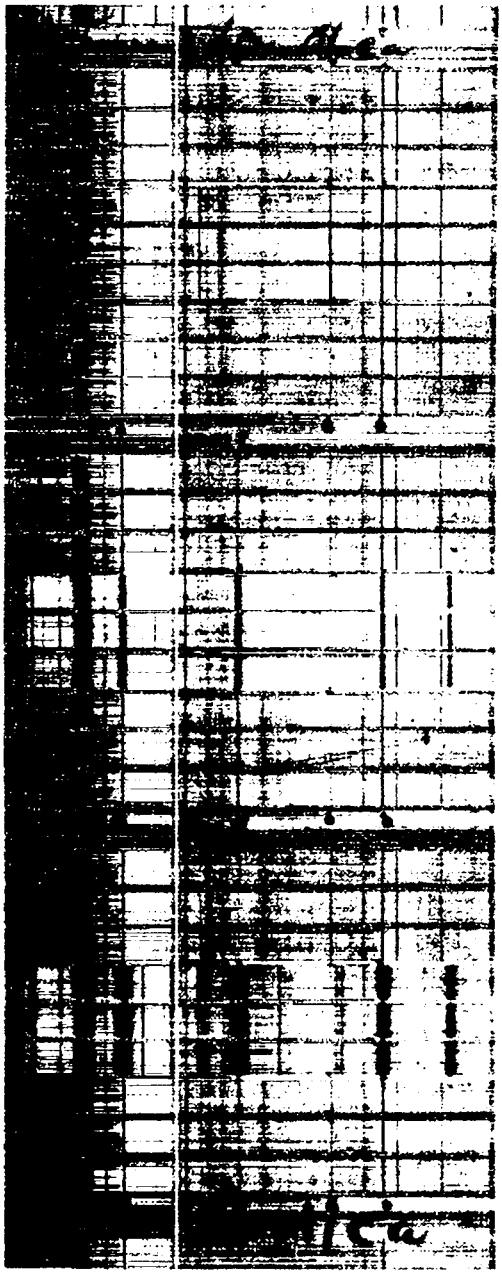

Figure 14

Typical Spectra of
Calcium, Aluminum, and Lanthanum

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