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**The Spectrophotometric Determination of
Microgram Quantities of Iron in
Plutonium Metal and Alloys**

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THE SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM
QUANTITIES OF IRON IN PLUTONIUM METAL AND ALLOYS

by

Thomas K. Marshall, Joel W. Dahlby, Glenn R. Waterbury

ABSTRACT

Iron, when present in concentrations between 0.35 and 30 ppm in electrorefined plutonium metal and its alloys or salts, is measured spectrophotometrically as ferrous orthophenanthroline following separation by liquid-liquid extraction. In the separation, iron(III) is extracted from an 8N hydrochloric acid solution of the plutonium into a dichloroethyl ether - carbon tetrachloride mixture. Then the iron is reduced and back-extracted into an aqueous phase containing hydroxylamine hydrochloride, sodium acetate buffer, and *o*-phenanthroline. The absorbance of the iron(II)-*o*-phenanthroline is measured at 510 m μ . Based upon 12 to 16 determinations each of 0.35, 0.696, 3.48, 6.96, 10.5, and 13.9 ppm of iron in plutonium, the relative standard deviations of the method were found to be 13.0, 11.7, 0.76, 0.37, 0.25, and 0.47%, respectively. From these data, a molar absorptivity of 10,700 was calculated. Of 54 ions tested, only antimony, gallium, silicon, and thallium interfere. Gallium, which is the only one of these elements often found in plutonium, can be eliminated by a pre-extraction step.

INTRODUCTION

A sensitive method was needed for measuring iron in concentrations between 0.35 and 30 ppm in electrorefined plutonium metal and its alloys or salts. Spectrophotometric methods have been published describing the extraction of iron from plutonium and measurement as iron(II) dipyriddy complex⁽⁶⁾ or bathophenanthroline.⁽⁵⁾ In another method currently used to analyze samples containing a minimum of 50 ppm of iron, plutonium(III) is precipitated as the oxalate followed by spectro-

photometric measurement of iron(II)-*o*-phenanthroline in the supernatant solution.⁽³⁾

The published methods for the extraction of iron from plutonium require that the iron be held quantitatively in the (II) oxidation state, which necessitates a holding reductant. In the dipyriddy method, "Teepol," a mixture of sodium alkyl sulfonates, was used to attain complete extraction of the iron. To avoid the difficulties involved in holding iron in its (II) oxidation state during the

extraction, the separation of iron as iron(III) was investigated.

Iron(III) acetylacetonate extracts into chloroform at pH 1. Some plutonium also extracts, and complexants, such as (ethylenedinitrilo) tetraacetic acid (EDTA), are ineffective in holding the plutonium in the aqueous phase at this pH. Iron(III) chloride is quantitatively extracted from strong hydrochloric acid into such organic reagents as ethyl ether, isopropyl ether, dichloroethyl ether, and methyl amyl ketone. Of these, dichloroethyl ether extracts 96% of the iron in one pass, ⁽⁴⁾ is safe to use in a dry box, and has a density greater than the aqueous phase, which facilitates repeated extractions to obtain quantitative separation of the iron. The separation of the phases was improved by mixing carbon tetrachloride with the dichloroethyl ether to increase the density of the organic phase.

It was found that the iron in the extract could then be back-extracted as iron(II) into an aqueous phase containing hydroxylamine, *o*-phenanthroline, and a buffer. This double extraction improved the separation of the iron and provided an aqueous phase for spectrophotometric measurement of the iron(II)-*o*-phenanthroline. Unfortunately, gallium interferes, but preliminary removal of this element is readily accomplished.

This report describes the preliminary separation of gallium, the double extraction separation of iron, and the spectrophotometric measurement as ferrous *o*-phenanthroline.

APPARATUS AND REAGENTS

Apparatus

Extraction apparatus, consisting of eight extraction vessels held by clamps which are attached as spokes in a wheel to a central collar or hub. This hub fits on the vertical, 1/2-in. - diam rod of a large ring stand made of Bakelite or phenolic board. The hub and extraction vessels can be rotated manually around the vertical rod. (See Fig. 1.) The tops of four of the extraction vessels are connected to vacuum by inserting one-hole, No. 3, rubber stoppers, that are attached to the vacuum line through rubber and glass tubing, a suitable manifold, and a safety bottle. The extrac-

tion vessels and the rubber stoppers are washed in hydrochloric acid prior to use to remove iron contamination.

Extraction vessel, borosilicate glass, consisting of a test tube, 150-mm long and 25-mm i. d., that has a tapered bottom to which a 1-mm capillary side arm is sealed as shown in Fig. 2.

Miscellaneous equipment. Normal laboratory glassware including volumetric flasks, pipets, beakers, and other equipment.

Spectrophotometer, Beckman Model DU or similar instrument, with glass or fused-silica cells having 1-cm light paths.

Syringe, 5-ml, Luer type, attached to a No. 3 rubber stopper.

Reagents

Acetone, reagent grade.

Ammonium hydroxide, 58%, reagent grade.

Boric acid, crystals, reagent grade.

Carbon tetrachloride, reagent grade.

Color solution. Dissolve 40 g of hydroxylamine hydrochloride, 20 g of sodium acetate, and 2 g of *o*-phenanthroline in water and dilute to 1 liter.

"Desicote," Beckman Instruments, Inc., or equivalent.

β , β' dichloroethyl ether, reagent grade. Redistill before using, collecting the fraction distilling in the range from 167° to 168°C (at an altitude of 7,300 ft), and store this fraction in a refrigerator.

Extracting solution. Mix 150 ml of dichloroethyl ether with 100 ml of carbon tetrachloride, add 50 ml of 8N hydrochloric acid, and shake for 1 min to saturate the organic phase with hydrochloric acid. Then allow the phases to separate, and remove the aqueous phase.

Hydrochloric acid, 12N, reagent grade.

Hydrochloric acid, 8N. Dilute 1.33 liter of 12N hydrochloric acid to 2.00 liter with distilled water. Add 50 ml of dichloroethyl ether and shake vigorously to extract any iron contamination. Allow the two phases to separate, and remove the dichloroethyl ether.

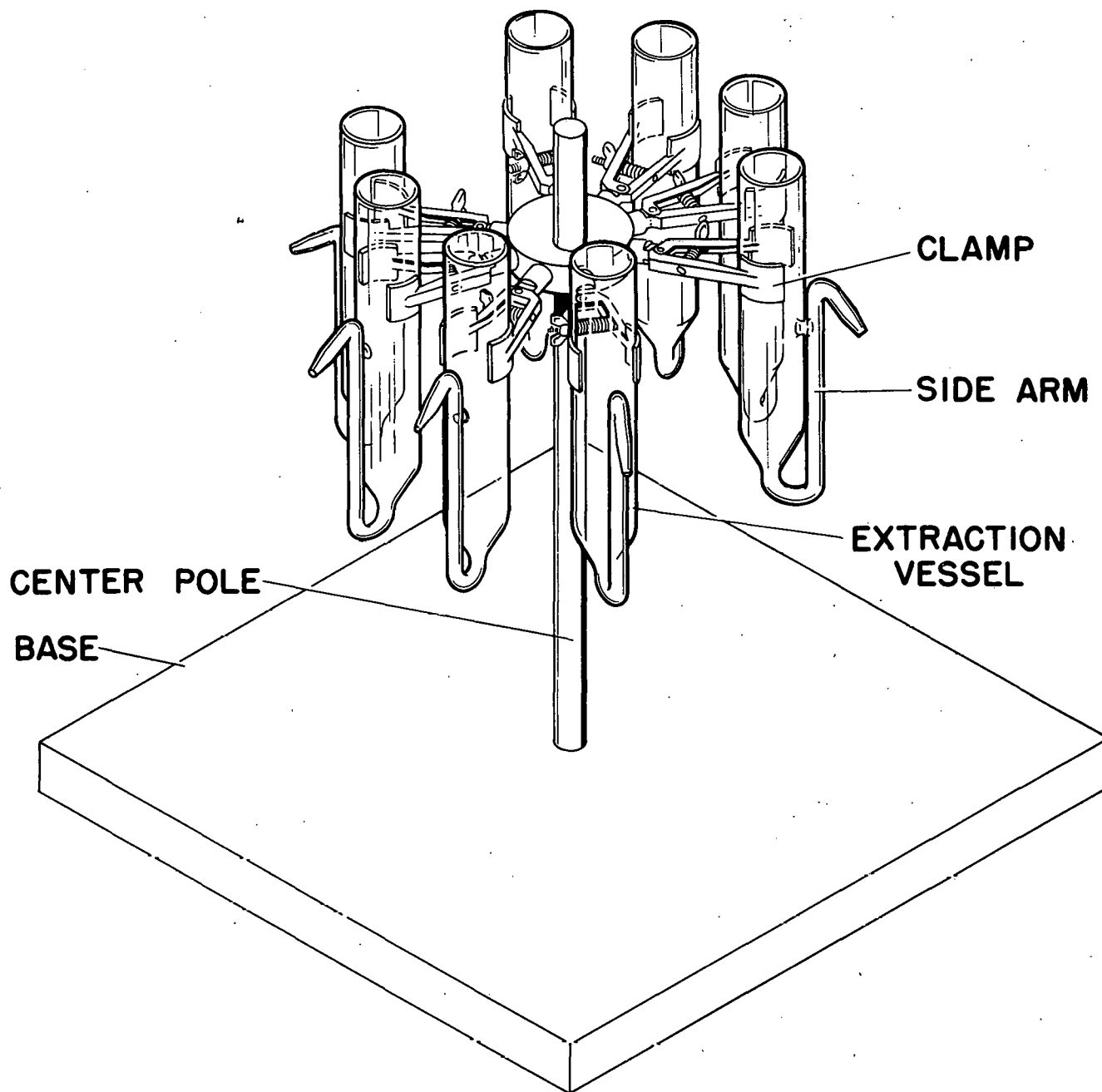


Fig. 1. Extraction apparatus.

Hydrochloric acid, 2N. Dilute 250 ml of 8N hydrochloric acid to 1 liter with distilled water.

Hydroxylamine hydrochloride, reagent grade (free of iron).

Iron solution, 7 $\mu\text{g}/\text{ml}$ of iron. Dilute 10 ml of iron stock solution to 500 ml with 8N hydrochloric acid.

Iron stock solution, about 350 $\mu\text{g}/\text{ml}$ of iron. Accurately weigh 350 mg of high purity iron wire, dissolve it in a minimum of 12N hydrochloric acid, and then dilute the solution to 1 liter with 2N hydrochloric acid.

Nitric acid, 70%, reagent grade.

pH indicating paper, "Hydrion Paper" or similar, for a pH range from 2 to 10.

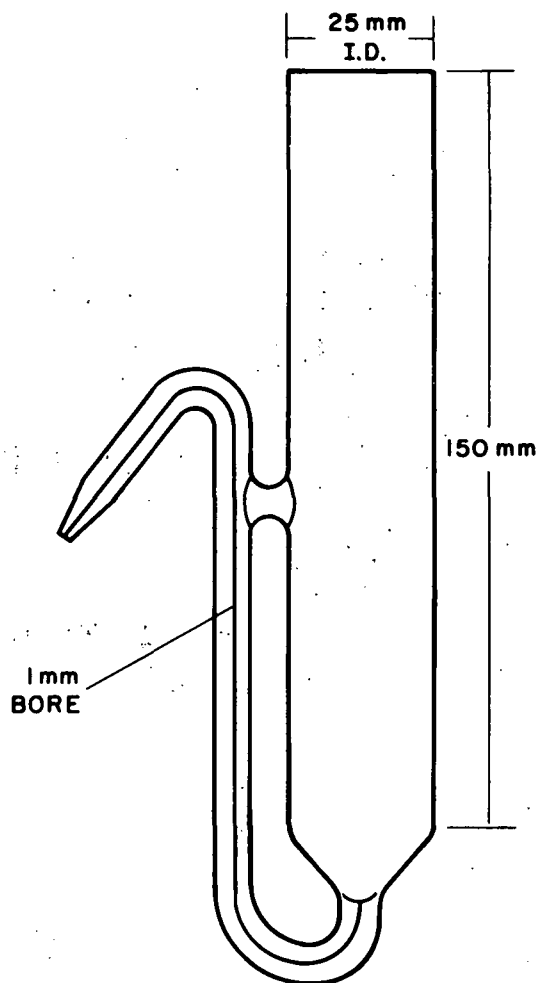


Fig. 2. Extraction vessel.

1, 10-phenanthroline (o-phenanthroline), reagent grade.

Sodium acetate, reagent grade.

Sulfuric acid, 36N, reagent grade.

Titanium(III) chloride, 20%, reagent grade.

SAMPLE PREPARATION

Solid Samples

The samples of plutonium metal or alloys are received as turnings or small pieces. Inspect the sample carefully and remove extraneous material, such as lint and foreign metal chips, that may have been introduced in the sampling or machining operations. If the sample is contaminated with cutting oil, wash the metal in methyl chloroform and dry at room temperature. Use appropriately sized

cuts of the washed sample for analysis. However, if the surface is oxidized and analysis of the entire sample, including oxide skin, is not requested, first clean the surface by filing or by pickling in dilute hydrochloric acid. Inspect other solid materials received as powders or as small pieces and remove extraneous materials. For high purity plutonium metal, accurately weigh two 2-g portions and transfer each to an extraction vessel. For less pure plutonium alloys or metals, weigh two portions that contain from 0.7 to 27.5 μg of iron and not more than 2 g of plutonium, and transfer each to an extraction vessel.

Add 2 ml of 12N hydrochloric acid dropwise to each sample to maintain a reasonable dissolution rate. When solution is complete, add 4 ml of 12N hydrochloric acid and then 8N hydrochloric acid to bring the total volume to 15 ml. Proceed to the RECOMMENDED PROCEDURE.

Solution Samples

Carefully inspect the solution and reject it if it contains solid residue. Use two aliquots each containing 0.7 to 27.5 μg of iron and not more than 2 g of plutonium. If the sample is a nitrate solution, add 1 ml of 36N sulfuric acid to each aliquot and evaporate to incipient dryness to remove nitrate which interferes with the method. Dissolve the residue in 15 ml of 8N hydrochloric acid. If the sample solution contains hydrofluoric acid, add 200 mg of boric acid to complex the fluoride and 12N hydrochloric acid to make the aliquot 8N in hydrochloric acid. Dilute the solution to 15 ml with 8N hydrochloric acid. If hydrochloric acid is the only acid in the aliquot, add hydrochloric acid and water to bring the normality to 8N and the volume to 15 ml. If the acid or iron concentration is too low to permit adjustment to the specified conditions, evaporate the aliquot to near dryness and then dissolve the residue in 15 ml of 8N hydrochloric acid.

RECOMMENDED PROCEDURE

Caution: Health safety rules for the handling of plutonium must be rigidly followed, and adequate protection for the operator must be ensured by the use of suitable dryboxes and protective clothing.

Analysis of Samples Containing Gallium

1. If the sample contains more than 200 ppm of gallium, prepare duplicate reagent blank and reference solutions by adding 6 ml of 12N hydrochloric acid, 3 ml of water, and aliquots containing various amounts (from 0 to 27.5 μg) of iron in 8N hydrochloric acid to extraction vessels. Then add sufficient 8N hydrochloric acid to each to make the final volume 15 ml.
2. Add 100 μl of a 20% titanous chloride solution to each reagent blank, reference, and sample solution.
3. Mix each solution well to reduce the iron(III) to iron(II), which will not extract, then add 5 ml of the extracting solution, and mix for 2 min. Allow the two phases to separate, and discard the organic phase which contains only gallium.
4. Add 50 μl of the titanous chloride and 5 ml of extracting solution to each solution. Perform a second extraction of the gallium as described in Step 3.
5. Repeat Step 4, then perform Steps 1 through 10 and Step 13 below.

Analysis of Samples That Do Not Contain Gallium

1. To each of four solutions in extraction vessels, add 2 drops of 70% nitric acid and mix to ensure that all iron(II) is oxidized to iron(III).
2. Add 5 ml of the extracting solution to each extraction vessel, connect the top of the vessel to vacuum, and mix the two phases for 2 min by drawing air through the solution. (While the first set of four extraction vessels are attached to the vacuum system, the second set may be readied for use. Then the second set are connected to the vacuum system while phases are separating in the first set.)
3. Disconnect the first set of four extraction vessels from vacuum, rotate the second set into position, and connect them to vacuum for 2 min to mix the two phases.
4. Allow the two phases to separate in each extraction vessel, use the 5-ml syringe connected to the top of the extractor through a rubber stopper to draw all liquid back from the side arm,

and then gently shake the extraction vessel to cause all of the organic liquid to combine into one continuous phase.

5. Use the syringe to force the organic layer out of each extraction vessel through the side arm, and collect the organic liquid in a 25-ml graduated cylinder.
6. Repeat Steps 2 through 5 twice to perform three extractions of the iron, and combine the organic phases from the three extractions in the 25-ml graduated cylinder. Then transfer the aqueous phase containing the plutonium or other radioactive solution to an appropriate residue container.
7. To the combined extracts in the graduated cylinder, add exactly 5 ml of the color solution, stopper the cylinder, and shake it for 1 min.
8. Allow the two phases to separate, and measure the pH of the aqueous phase with pH paper. If the pH is not 4, add 1 or 2 drops of concentrated ammonium hydroxide to adjust the pH to 4.
9. Shake the solution for another 30 sec and then allow to stand for 30 min for color development.
10. Pipet a portion of the aqueous phase into a spectrophotometer cell having a 1-cm path-length, and measure the absorbance of the iron (II)-o-phenanthroline complex at a wavelength of 510 $m\mu$ using water as a reference solution.
11. Determine a reagent blank by adding 6 ml of 12N hydrochloric acid, 3 ml of water, and 6 ml of 8N hydrochloric acid to the extraction vessel and performing Steps 1 through 10. Subtract the absorbance of the reagent blank, A_b , from the absorbance of the sample solution, A_s , to obtain the corrected absorbance.
12. Obtain data for a standard curve by analyzing solutions, containing known quantities of iron from 0.7 to 27.5 μg , according to Steps 1 through 11.
13. Plot the corrected absorbances as a function of the iron contents. Read from the standard curve the micrograms of iron (Fe, μg) corresponding to the corrected absorbance for the sample, and calculate the iron concentration using Eq. (1)

for solid samples or Eqs. (2) and (3) for solutions.

$$\text{Fe, ppm} = \frac{\text{Fe, } \mu\text{g}}{\text{Sample wt, } g} \quad (1)$$

$$\text{Fe, } \mu\text{g/ml} = \frac{\text{Fe, } \mu\text{g}}{\text{Volume of aliquot, ml}} \quad (2)$$

$$\text{Fe, ppm} = \frac{\text{Fe, } \mu\text{g/ml}}{g/\text{ml of sample}} \quad (3)$$

EXPERIMENTAL

Selection of the Organic Extractant for Iron(III)

Morrison and Freiser⁽⁴⁾ list organic solvents, such as ethyl ether, isopropyl ether, methyl isobutyl ketone, and dichloroethyl ether, for the extraction of iron(III) from hydrochloric acid solutions. Flash points of these solvents are -20° , -18° , 73° , and 131°F , respectively, showing that ethyl ether and isopropyl ether are unsafe to use in a drybox. Dichloroethyl ether and methyl isobutyl ketone are relatively safe and are efficient extractants for iron(III). Dichloroethyl ether was selected for the present application because of its higher flash point and also because it has a higher density than methyl isobutyl ketone (1.222 as compared to 0.801). It is advantageous for the organic phase to have a higher density when several repeated extractions are made because of the easy removal of the bottom layer from the extraction vessel used.

Tests of the efficiency of dichloroethyl ether as an extractant for iron(III) from 8N hydrochloric acid showed that the extraction of 8.0 μg and 10.2 μg was essentially complete in two passes using an organic volume equal to one third of the aqueous phase in each pass (Table I). A diluent, such as methyl isobutyl ketone or carbon tetrachloride, had to be added to the dichloroethyl ether to obtain quantitative back-extraction of the iron into the aqueous color-forming solution. Although methyl isobutyl ketone was effective in this respect, this diluent proved unsatisfactory because some of the sodium acetate buffer passed from the color solu-

tion into the organic phase. The net effect was an increase in the acidity of the aqueous phase that inhibited quantitative formation of the iron(II) *o*-phenanthrolate.

Carbon tetrachloride proved effective in causing release of iron from the dichloroethyl ether to the aqueous back-extractant, and there was no deleterious effect. In fact, the high density of carbon tetrachloride provided an additional advantage when microgram quantities of iron were separated from 2 g of plutonium. The large amount of plutonium increased the density of the aqueous phase so that the phases did not separate cleanly. Addition of 1 volume of carbon tetrachloride to 1.5 volumes of dichloroethyl increased the density of the organic phase and significantly improved the separation of the two phases. This separation was further enhanced by adding 5 ml of 8N hydrochloric acid to dilute the 10 ml of aqueous phase to reduce its density. All further extractions were made under these conditions. The extraction of either 7.0 μg or 13.9 μg of iron was essentially complete in two passes using an organic volume equal to one-third of the aqueous volume in each pass (Table I).

Back Extraction of Iron(II) as the *o*-Phenanthrolate

In the development of the iron(II)-*o*-phenanthrolate color in aqueous solutions, *o*-phenanthroline, sodium acetate as a buffering agent, and hydroxylamine hydrochloride as a reducing agent are commonly added. The order of addition of these reagents and careful adjustment of the pH to 4⁽¹⁾ reportedly are critical parameters. It was found that 5 ml of sodium acetate buffer, containing 20 g/liter of sodium acetate, adequately adjusted the pH of the aqueous back-extraction phase to 4 without the addition of either acid or base.

The simultaneous addition of buffer, reductant, and chromogenic agent was shown to be satisfactory by comparing the molar absorptivity obtained following the simultaneous addition of reagents with the reported value resulting from the sequential addition of the various reagents. The simultaneous addition of reagents was accomplished by preparing one solution containing 40 g of hydroxylamine hydrochloride, 20 g of sodium acetate,

TABLE I
Efficiency of the Extraction of Iron(III) From 8N Hydrochloric Acid Into
Dichloroethyl Ether And Into Dichloroethyl Ether - Carbon Tetrachloride

Solvent	Fe Taken, μg	Extraction (Pass)	Fe Extracted, %	Total Fe Extracted, %
Dichloroethyl ether	8.0	1st	94.5	94.5
		2nd	5.1	99.6
		3rd	0.3	99.9
	10.2	1st	94.9	94.9
		2nd	4.5	99.4
		3rd	0.4	99.8
4th		0.2	100.0	
Dichloroethyl ether - carbon tetrachloride	7.0	1st	89.3	89.3
		2nd	10.7	100.0
		3rd	0.0	100.0
	13.9	1st	86.9	86.9
		2nd	12.9	99.8
		3rd	0.2	100.0

and 2 g of *o*-phenanthroline per liter. Five-ml aliquots of this solution were used as the color-forming reagent and back extractant for the iron from the dichloroethyl ether-carbon tetrachloride phase. An average molar absorptivity of 10,700 was obtained for the aqueous phase under these conditions as compared to 11,100 reported⁽²⁾ following sequential additions of the reagents. The organic phase had essentially no absorbance at a wavelength of 510 m μ , showing that the decrease in the molar absorptivity probably is a result of incomplete color formation rather than partial back extraction of the colored species into the aqueous phase. Although the molar absorptivity is slightly low, it is quite reproducible, and the simultaneous addition of reagents seems satisfactory as well as convenient.

To determine the optimum time required for the color development, 13.9 μg of iron was extracted into the mixed organic solvent and back-extracted into the color-forming reagent, and the absorbance of the aqueous phase was measured repeatedly following known time intervals. Three min after the back extraction, the absorbance was about 6% higher than the value measured after 10 min. From this point in time, the absorbance

remained essentially constant for 24 hr. The initial decrease in absorbance during the first 10 min probably is a result of settling out of organic droplets and a reduction in cloudiness of the aqueous phase. The data show that 10 to 15 min probably are adequate for complete separation of the phases. To ensure complete separation in all cases, a waiting period of 30 min is recommended.

Effect of Plutonium

The largest practical sample size was investigated by determining iron, according to the RECOMMENDED PROCEDURE, in solutions containing either 1, 2, or 3 g of plutonium and 13.9 μg of iron. Reagent blanks also were determined for all reagents including the plutonium solution. It was found that the plutonium metal contained between 1 and 8 ppm of iron which made the absorbances high and interfered with measurement of any small effects that might be caused by the plutonium. Therefore an iron-free plutonium solution was prepared by adding hydrochloric acid to the plutonium solution to make the acidity 8M, adding a few drops of nitric acid to oxidize the iron(II), and then extracting the iron(III) into dichloroethyl ether - carbon tetrachloride. Six extractions were made to ensure complete removal. The measurements

of reagent blanks and known quantities of iron added to the plutonium were repeated (Table II) using the iron-free plutonium solution. The results show that the largest practical sample size is 2 g.

Effect of Gallium

In the course of the investigation of the effects of other elements (ions), it was surprising to find that gallium caused very low results for iron. As plutonium often is alloyed with gallium, its removal, or the masking of its interference, was essential unless the applicability of this method was to be limited to analysis of high purity plutonium only.

The effect of gallium on the extraction of iron was investigated by performing three extractions of 13.9 μg of iron from 8M hydrochloric acid solutions containing 100 mg of gallium. The aqueous phases were evaporated to dryness, and the residues were dissolved in the o-phenanthroline color solution. Formation of an iron(II)-o-phenanthrolate color showed that the extraction was incomplete. Addition of the color solution to the combined organic phases with mixing failed to produce the characteristic red color. An additional 7 μg of iron were added to the combined organic phases, the pH was carefully adjusted by adding ammonium hydroxide, and the mixture was shaken again. The iron(II)-o-phenanthrolate color still did not form. These tests showed that gallium interfered with the extraction of iron and also with the color development.

Several masking agents or complexants, such as (ethylenedinitrilo) tetraacetic acid, were added to prevent the interference caused by gallium, but none was successful. Therefore, separation of the gallium before the extraction of the iron was investigated. A search of the literature showed that the separation most promising for the solutions involved would be the extraction of gallium (III) from 8M hydrochloric acid into dichloroethyl ether - carbon tetrachloride while iron was held in the (II) oxidation state. Of the several reductants tried as holding agents for the iron(II), titanium(III) was the most effective. It also had the advantage of being readily oxidized by nitric acid.

In this way, the titanium(III) and iron(II) could be oxidized easily prior to the extraction of iron(III). For plutonium solutions freshly prepared from the metal, the plutonium was essentially all in the (III) oxidation state which did not consume titanium(III), and the iron was effectively held in the (II) oxidation state by adding a small quantity of titanium(III) chloride solution. If significant amounts of the plutonium were in higher oxidation states, more titanium(III) solution was required, and the reagent blank was significantly increased because of the iron in this reagent. Titanous chloride solutions, either prepared from titanium metal or commercially available, were found to be contaminated with iron. Therefore a minimum quantity was added, and this was accurately measured. Two hundred μl of 20% titanous chloride solution was adequate to reduce microgram amounts of iron. The absorbance caused by the iron in this quantity of solution was about 0.130 in addition to the reagent blank absorbance of 0.015 in the absence of titanium.

Solutions containing either 3.64 or 19.8 μg of iron, 100 mg of gallium, and 1 g of plutonium in the (III) oxidation state, and suitable reagent blank solutions, were analyzed in the following manner. The iron was reduced by adding 200 μl of 20% titanous chloride solution, and the gallium was extracted in three passes into dichloroethyl ether - carbon tetrachloride. Then 2 drops of 70% nitric acid were added to oxidize the iron which was extracted and measured spectrophotometrically as described in this method. The results (Table III) show that prior extraction of the gallium is effective in removing this interfering ion; the average of the values for the iron found is 99% of the true amount. The iron contamination resulting from the addition of the titanous chloride is indicated by the average absorbance of 0.146 for the reagent blank, and the absence of interference from 100 mg of gallium is shown by the fact that the two reagent blank absorbances are essentially equal. The prior extraction of gallium was included in the method and was used in all subsequent determinations if gallium was a known or suspected contaminant of the sample.

TABLE II

Effect of Plutonium on the Measurement of Iron

Fe Added, <u>μg</u>	Pu Added, <u>g</u>	Number of <u>Determinations</u>	Av. Absorbance <u>510 $m\mu$</u>
0.0	0	4	0.012
13.9	0	8	0.554
0.0	1	2	0.013
13.9	1	2	0.549
0.0	2	13	0.015
13.9	2	14	0.552
0.0	3	2	a
13.9	3	2	a

^aOrganic and aqueous phases did not separate cleanly.

RELIABILITY

The precision of the method was determined by making at least 12 measurements of each of six iron concentrations according to the RECOMMENDED PROCEDURE. These solutions also contained 2 g of plutonium. The plutonium stock solution was made iron-free by six successive extractions into dichloroethyl ether as described previously. A comparison of the absorbances of the reagent blanks measured for solutions without plutonium (0.012) and for solutions that contained 2 g of plutonium (0.015) indicated that the iron had been effectively removed. The results (Table IV) show that the relative standard deviation is 12 to 13% in measuring 0.35 ppm of iron and 0.8% or less in measuring 3.5 to 13.9 ppm (6.96 to 27.8 μg of Fe). The differences from 100% in the values for the iron found in measuring 0.35 and 0.70 ppm do not show a bias in the method but are indicative of the poorer precision at these low levels. From the average absorbance per microgram of iron of 0.0384, a molar absorptivity of 10,700 was calculated.

The effects of 54 other elements (ions) on this method were determined (Table V) by adding 50 to 1750 mg of the ion to a solution containing 13.9 μg of iron, and then analyzing for the iron as described. Of these elements, only antimony, gallium,

silicon, and thallium interfere at the 50- mg level. The interference caused by antimony and thallium was not studied because these elements are not common impurities in plutonium. Although silicon is a common contaminant in plutonium, the low silicon content of most plutonium would not cause interference. Larger concentrations of silicon can be removed from the solution of a sample by adding hydrofluoric and sulfuric acid and heating until sulfur trioxide fumes are evolved. The interference caused by gallium is serious because plutonium frequently is alloyed with this element. The preliminary extraction of the gallium to remove this interference is discussed under Analysis of Samples Containing Gallium and also under Effect of Gallium.

The method has been applied successfully to the measurement of iron in various high purity plutonium metals and alloys, and to other materials such as sodium metal contaminated with plutonium. The method proved especially advantageous in measuring iron in cobalt-containing plutonium alloys and in materials contacted with these alloys. Approximately 16 analyses can be performed in duplicate in 8 hr.

TABLE III

Results for Iron Following Removal of Gallium

Fe Added, <u>μg</u>	Ga Added, <u>mg</u>	Pu Added, <u>g</u>	Number of <u>Determinations</u>	Av. Absn., <u>510 mμ</u>	Fe Found, <u>%</u>
0.00	0.0	0	4	0.147 ^a	-
0.00	100.0	0	4	0.145 ^a	-
3.64	100.0	1	4	0.278	95
3.64	0.0	1	4	0.285	100
19.8	100.0	1	2	0.910	100
19.8	0.0	1	2	0.917	101

^aA high reagent blank absorbance results from iron in 200 μl of titanous chloride solution.

TABLE IV

Reliability of the Measurement of Iron in Two Grams of Plutonium

Fe Taken, <u>μg</u> <u>ppm</u>		Number of <u>Determinations</u>	Fe Found, <u>μg^a</u>	Fe Found, <u>%</u>	Rel Std Dev, %
0.00		12	-	-	-
0.7	0.35	14	0.6	86	13.
1.4	0.70	15	1.6	114	12.
7.0	3.5	12	6.9	99	0.76
13.9	7.0	14	14.0	101	0.37
20.9	10.5	15	20.9	100	0.25
27.8	13.9	16	28.0	101	0.47

^aBased upon the average absorbance per μg of Fe of 0.0384 obtained for all of the measurements.

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TABLE V

Effects of Various Elements on the Determination of Iron
(13.9 μg of iron in each determination)

<u>Quantity Added, mg</u>	<u>Noninterfering Elements (Ions)^a</u>	<u>Interfering Elements (Ions)</u>
100	Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Na, Nb, Ni, Pb, Pd, Pt, Rb, Ru, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, U, V, W, Y, Zn, Zr	Ga, Mo, Sb, Si, Tl
50	Mo	Ga, Sb, Si, Tl
1750	SO_4^{2-}	
1250	ClO_4^{1-} ^b	
550	F^{1-} ^c	
300	NO_3^{1-}	

^aThe added ion did not change the results for Fe by more than 3%.

^bDid not interfere when each 5-ml extract was washed with 10 ml of 8N HCl.

^cDid not interfere when complexed with 200 mg of boron.