

STUDY ON THE DETERMINATION OF TRACES OF IMPURITIES IN URANIUM METAL AS NUCLEAR FUEL

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1. Introduction

Uranium metal as nuclear fuel contains various kinds of impurities, which they are classified as follows:

a) Elements with a high thermal neutron cross section. They must be absent in nuclear fuel, and the following elements belong to this group. Boron, cadmium, rare earths, lithium, silver, cobalt etc. The neutron absorption degree of these elements is shown in Table 1.

b) Elements of much influence on metallurgical property. Among these there are carbon, nitrogen, oxygen etc.

c) Other elements of little influence on nuclear fuel.

Accordingly, the determination of impurities is importance on the production of uranium metal as nuclear fuel. Impurities are present in concentrations of parts per million and determined by the usual method of analysis with difficulty. Therefore, a simple and precise methods have been urgent to determine traces of impurities in uranium metal. Since 1958 our laboratory has studied and develop-

TABLE 1. Thermal Neutron Absorption by Impurities

Element	K(U)*	ppm/0.001% A	Element	K(U)*	ppm/0.001% A
Gd	9077	0.0011	Re	14.0	0.71
B	2160	0.0046	Ho	12.0	0.83
Sm	1132	0.0038	Kr	10.3	0.97
Eu	937	0.011	H	10.1	0.99
Cd	702	0.014	Nd	9.9	1.0
Li	317	0.032	Tb	8.5	1.2
Dy	210	0.048	Xe	8.3	1.2
Ir	68.9	0.15	Mn	7.4	1.4
Hg	58.6	0.17	Cs	6.7	1.5
In	51.3	0.19	Yb	6.4	1.6
Rh	45.1	0.22	Se	4.6	2.2
Er	30.7	0.33	Ne	4.3	2.3
Cl	27.6	0.36	N	4.1	2.4
Tm	21.5	0.47	Ta	3.7	2.7
Co	19.4	0.52	Ti	3.6	2.8
Lu	19.1	0.52	W	3.2	3.1
Hf	18.2	0.55	V	3.1	3.2
Ag	17.8	0.56	Br	2.6	3.8
Sc	16.5	0.61	Pr	2.5	4.0
Au	15.4	0.65	Ni	2.4	4.2

TABLE 1 (continued)

Element	K(U)*	ppm/0.001% A**	Element	K(U)*	ppm/0.001% A**
Os	2.4	4.2	Y	0.48	21
Pb	2.3	4.3	S	0.47	21
La	2.0	5.0	Sr	0.41	24
Cu	1.8	5.6	Nb	0.37	27
Cr	1.7	5.9	Ca	0.33	30
As	1.7	5.9	Ba	0.26	38
I	1.6	6.3	Al	0.26	38
K	1.6	6.3	Rb	0.25	40
Sb	1.4	7.1	P	0.19	53
Fe	1.4	7.1	Sn	0.16	63
Pt	1.3	7.7	Ce	0.16	63
Ga	1.2	8.3	Si	0.14	71
Te	1.1	9.1	Mg	0.080	123
Ge	1.0	10	Zr	0.061	163
U	1.000	—	He	0.054	185
Th	0.94	11	Be	0.034	294
Mo	0.81	12	Pb	0.025	400
Ru	0.75	13	F	0.016	625
Na	0.69	15	C	0.0083	1200
Zn	0.50	20	D	0.0071	1400
Tl	0.50	20	Bi	0.0047	2100
A	0.48	21	O	0.0004	2500

* Thermal neutron absorbed by the impurity relative to the absorption by an equivalent weight of uranium.

** Concentration in parts per million (uranium basis) which gives a thermal neutron absorption of 0.001% relative to uranium.

ed methods for various elements. Among these spectrophotometric, polarographic, coulometric, X-ray spectrometric, spectrographic and other methods are contained.

In this paper, our study on the determination of traces of impurities in uranium metal is summarized.

2. Analytical Procedures and Results

2.1. Spectrophotometric method

2.1.1. Apparatus

Shimadzu photoelectric spectrophotometer QR 50 was used for measuring absorbance of the solution throughout this study.

2.1.2. Arsenic

A sample was decomposed with nitric and perchloric acids, and arsenic in the solution was extracted with carbon tetrachloride after reduction with iodide. Arsenic was then back-extracted into water and, after oxidation to quinquevalent state, converted to molybdiarsenate which was extracted into methyl isobutylketone. Molybdiarsenate was reduced in the organic phase to strongly colored molybdenum blue and determined photometrically.

PROCEDURE

Sample (1 g):

[Dissolve the sample in 5 ml of HNO₃,

Add 3 ml of HClO_4 (60%) to it,
 Evaporate and fume it for 2 minutes,
 Cool and add 2 ml of water to it,
 Add 15 ml of HCl and 1 ml of potassium iodide solution (5%) to the solution to reduce arsenic,
 Transfer the solution to 100 ml separatory funnel,
 Extract arsenic by shaking with 20 ml of carbon tetrachloride for 1 minute,
 Reserve the organic phase and repeat the extraction of arsenic from aqueous phase,

Combined organic phase:

Back-extract arsenic into 30 ml of water,

Aqueous phase:

Add 5 ml of perchloric acid (60%) to the aqueous phase,
 Add potassium permanganate solution (1%) dropwise to the solution until faintly pink color remains,
 Add 3 ml of ammonium molybdate solution (10%) to it,
 Shake and stand it for 5 minutes,
 Extract molybdiarsenate into 15 ml of methyl isobutylketone,
 Discard the aqueous phase and wash the organic phase with 10 ml of HCl (1+20) two times,
 Transfer the organic phase to a 20 ml volumetric flask,
 Add 4 ml of ethanol (99%) and 0.15 ml of stannous chloride solution (50 g in HCl (1+1)) to the flask,
 Dilute it with ethanol (99%) to the mark and stand it for 20 minutes,
 Measure the absorbance of the solution at 735 $m\mu$ against a mixture of methyl isobutylketone and ethanol (3+1) as a reference solution.

Calibration curve is prepared by treatment of known amounts of arsenic as the above procedure except the preliminary extraction with carbon tetrachloride.

NOTES

- 1) This method serves to determine 2-50 ppm of arsenic.
- 2) Arsenic (III) is effectively extracted with carbon tetrachloride in the presence of perchloric and hydrochloric acids.

The calibration curve is shown in Fig. 1 and the results obtained for uranium sample are shown in Table 2.

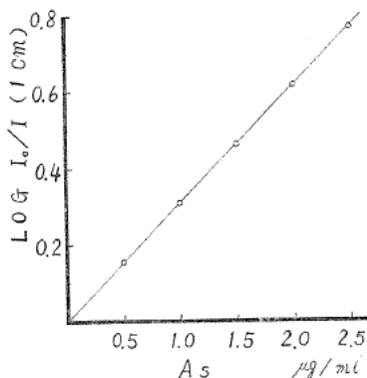


FIG. 1. Determination of arsenic by the molybdenum blue method.

TABLE 2. Determination of Arsenic by the Proposed Method

Arsenic added (ppm)	Phosphorus added (ppm)	Arsenic found (ppm)
—	—	2.0, 2.3, 2.1
—	100	2.4
20.0	200	22.0
30.0	—	31.8

2.1.3. Boron

Method I: A sample was dissolved in hydrochloric acid and hydrogen peroxide, and the solution thus obtained was evaporated with sulfuric acid until fumes of sulfuric acid were evolved. Boron was isolated by distillation as methyl borate and determined photometrically by the curcumin method.

PROCEDURE

Sample (1 g):

- Place the sample in a quartz distillation flask (Fig. 2),
- Add 2 ml of water and 2 ml of HCl (6 N) to the flask,
- Start the reaction with a gentle flame,
- Add 2 ml of H₂O₂ (15%) to the flask,
- Continue heating after the initial reaction subsides,
- Cool and add 1.5 ml of H₂SO₄ to the flask,
- Evaporate it until fumes of sulfuric acid are evolved,
- Cool it and connect the flask to the still (receiving dish contains 3 ml of Ca(OH)₂ solution (3%)),
- Place a beaker of cold water so as to envelop the distillation flask and place a beaker of hot water (80°C) so as to envelop methanol flask,
- Stop the heating of methanol flask when 25 ml of methanol is distilled in the distillation flask,
- Heat the distillation flask by surrounding with a beaker of hot water (90°C) and finally, heat to boiling until no more alcohol distills,
- Repeat the above manipulation once more,
- Wash the end of the condenser tube with water,
- Add 20 ml of water in the receiving dish,
- Evaporate the solution on a water bath,
- Cool and acidify it with HCl (3 N),
- Add 4 ml of curcumin-oxalic acid solution (0.040 g of curcumin and 5 g of oxalic acid in 100 ml of ethanol) to the dish,
- Evaporate the mixture to complete dryness in a water bath kept at 55 ± 3°C,
- Coll it to room temperature and extract the residue with 10 ml of ethanol,
- Stir and centrifuge the mixture at 3000 rpm for 10 minutes,
- Measure the absorbance of the solution at 540 mμ,
- Correct it for blank and recovery of boron.

Calibration curve is prepared by direct color development of known amounts of boric acid (0 to 0.4 μg).

NOTES

1) Recovery of boron in the presence of uranium was 90% and recovery without uranium was thought to be 100%.

2) Calcium hydroxide solution seemed so superior to sodium hydroxide solution as a receiving solution for methyl borate, since the reproducibility and sensitivity in the color development by curcumin were higher in the presence of calcium salt rather than in the presence of sodium salt.

3) This method was suitable for the determination of 0.1-0.5 ppm of boron. The distillation apparatus for boron is shown in Fig. 2, and the calibration curve is shown in Fig. 3.

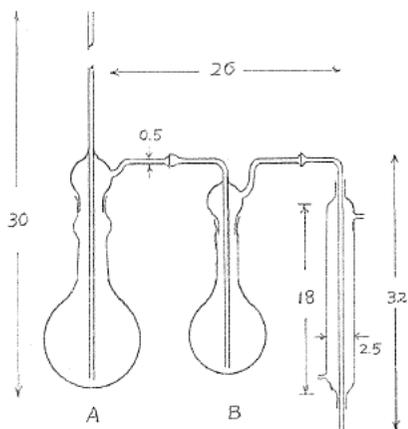


FIG. 2. Boron distillation apparatus: A. methanol flask (150 ml), B. distillation flask (100 ml).

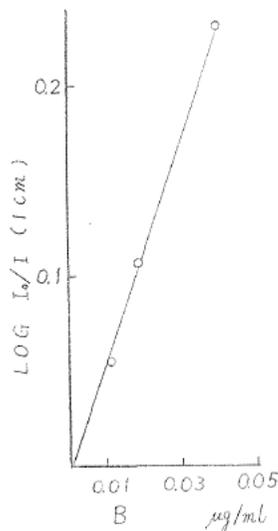


FIG. 3. Determination of boron by the curcumin method.

Method II: A sample was dissolved in hydrochloric acid and hydrogen peroxide, and boron was isolated by distillation as methyl borate and determined photometrically by the curcumin method.

PROCEDURE

Sample (1 g):

- Place the sample in a distillation flask (Fig. 4),
- Add 2 ml of HCl (1+1) to the flask,
- Connect the flask to the air condenser and heat the sample to decompose,
- Add 2 ml of hydrogen peroxide to complete solution to the flask,
- Cool and add 10 ml of methanol to the flask from a top of condenser,
- Remove the flask from the condenser and connect the flask to the still (receiving platinum dish contains 2.0 ml of sodium hydroxide solution (5%) and 5 ml of methanol),
- Immerse the flask in a beaker of $80 \pm 2^\circ\text{C}$ water,
- Distill the methyl borate while introducing dried air of 30 ml/minutes,
- Continue to distil until 3-4 ml of solution remains in the distillation flask,

Cool, add 10 ml of methanol in the distillation flask and repeat the distillation procedure,
 Evaporate the distillate to dryness on a water bath,
 Add 1.0 ml of water to the residue and neutralize with HCl (1+1) using phenolphthalein as an indicator,
 Add 2.0 ml of curcumin-oxalic acid-methanol solution to it,
 Evaporate the mixture on a water bath, kept at $55 \pm 0.5^\circ$, while introducing dried air of 4.0-4.3 l/minutes,
 Allow it to remain there until no odor of HCl is left,
 Extract the residue with methanol,
 Filter the methanol solution through a glass filter and wash the residue on a glass filter with methanol,
 Dilute the filtrate to 15 ml using a volumetric flask,
 ↓ Measure the absorbance of the solution at 540 m μ .
 Calibration curve is prepared by adding known amounts of boric acid to 6.7 ml of sodium hydroxide solution (5%) and taking through the distillation.

NOTE

This method serves to determine more than 0.1 ppm of boron.

The apparatus used for Method II is shown in Fig. 4.

The results shown in Table 3 were obtained by the above procedures.

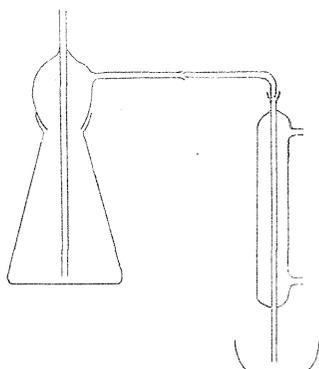


FIG. 4. Boron distillation apparatus.

TABLE 3. Determination of Boron by the Proposed Methods

Sample	Boron found (ppm)	
	Method I	Method II
A	0.11, 0.10, 0.09, 0.10	—
B	0.12	0.09, 0.10, 0.10
C	0.15	0.14
D	—	0.24*

* standard value 0.23 ppm.

2.1.4. Cadmium

Method I: A solution of uranium metal was treated with dithizone-carbon tetrachloride solution to remove copper and with dimethylglyoxime-chloroform solution to remove nickel. Then, cadmium was extracted as dithizone complex with dithizone carbon tetrachloride solution after addition of hydroxylamine hydrochloride and a large amount of ammonia. Lead and zinc in the extract were removed by washing the extract with sodium hydroxide solution. Cadmium was back-extracted into dilute hydrochloric acid and re-extracted from sodium hydroxide solution with dithizone-carbon tetrachloride solution.

PROCEDURE

Sample (2.5 g):

Decompose the sample with 10 ml of HCl (6 N),

Oxidize uranium with 2.5 ml of H_2O_2 (30%),
Evaporate the solution to dryness on a water bath,
Add 10 ml of HCl (N/100) to dissolve the residue,
Transfer the solution to 100 ml separatory funnel,
Add 1 ml of hydroxylamine hydrochloride solution (10%) to it,
Shake the solution with 5 ml of dithizone-carbon tetrachloride (0.05%) to
remove Cu etc.,
Reject the organic phase and remove completely dithizone in aqueous
phase by shaking with carbon tetrachloride,
Add 10 ml of sodium citrate solution (50%), 2 ml of dimethylglyoxime
solution (1% in sodium hydroxide solution (1%)) and 3.0 ml of am-
monia to the aqueous phase,
Extract nickel-dimethylglyoximate with 5 ml of chloroform for 1 minute,
Reject the organic phase and wash the aqueous phase with 5 ml of carbon
tetrachloride,
Add 20 ml of ammonia to the aqueous phase,
Extract cadmium as dithizonate by shaking with 5 ml of dithizone-carbon
tetrachloride (0.05%) and repeat the extraction until the organic phase
shows no color,

Organic phase:

Transfer the organic phase to another 50 ml separatory funnel,
Back-extract cadmium by shaking with 10 ml of HCl (N/100) and 0.5 ml
of hydroxylamine hydrochloride (10%) to separate the oxidation
product of dithizone,

Aqueous phase:

Add 1 ml of sodium citrate solution (10%) and 4 ml of sodium hydroxide
solution (20%) to the aqueous phase,
Extract cadmium as dithizonate by shaking with 5.00 ml of dithizone-
carbon tetrachloride solution,

Measure the absorbance of the extract at 520 m μ ,

↓ Correct the reagent blank.

Calibration curve is prepared by carrying standard solution through the
entire procedure.

NOTES

- 1) Reagents should be purified from impurities.
- 2) This method is suitable for the determination of 0.05–1 ppm of cadmium.

Method II: A sample was decomposed with hydrochloric acid and hydrogen
peroxide, and cadmium was separated by extraction as an iodo-complex followed
by the photometry with dithizone.

PROCEDURE

Sample (5 g):

Decompose the sample with 20 ml of HCl (1+1),
Oxidize uranium with 5 ml of H_2O_2 (30%),
Evaporate the solution almost to dryness,
Add 15 ml of water to dissolve the salt,
Add 1 ml of hydroxylamine hydrochloride solution (10%), and stir the solution,
Add 10 ml of potassium iodide solution (3 M), 25 ml of trisodium citrate

solution (50%) and 3 ml of sodium thiosulfate solution (1 M) to it,
 Adjust the pH of the solution to 6-8 with ammonia,
 Transfer the solution to 100 ml separatory funnel,
 Extract the iodo-complex of cadmium by shaking with 25 ml of methyl
 isobutylketone for 1 minute,
 Reserve the organic phase and repeat the extraction procedure two times,

Combined organic phase:

Back-extract cadmium with 10 ml of water three times,

Aqueous phase:

Transfer the aqueous phase to 100 ml separately funnel,
 Add 1 ml of hydroxylamine hydrochloride solution (10%), 1 ml of trisodium
 citrate solution (10%) and 10 ml of sodium hydroxide solution (20%)
 to it,
 Extract cadmium by shaking with 10 ml of dithizone-carbon tetrachloride
 solution for 1 minute,

Organic phase:

Transfer the organic phase to 50 ml separatory funnel,
 Back-extract cadmium with a mixture of 10 ml of HCl (N/100) and 0.5
 ml of hydroxylamine hydrochloride solution (10%),
 Discard the organic phase and wash the aqueous phase with 5 ml of carbon
 tetrachloride two times,

Aqueous phase:

Add 1 ml of trisodium citrate solution (10%) and 4 ml of sodium hydro-
 xide solution (20%) to the aqueous phase,
 Extract cadmium with 5 ml of dithizone-carbon tetrachloride solution
 (0.005%),

↓ Measure the absorbance of the organic phase

Calibration curve is prepared by extraction of cadmium dithizone complex
 without methyl isobutylketone extraction.

NOTES

1) It was examined using ^{115m}Cd that more than 90% of cadmium was
 recovered by methyl isobutylketone extraction three times.

2) This method serves to determine more than 0.02 ppm of cadmium.

The results obtained by the proposed methods are shown in Table 4.

Calibration curve obtained by Method I is shown in Fig. 5.

TABLE 4. Determination of Cadmium by the Proposed Methods

Sample	Cadmium added (ppm)	cadmium found (ppm)	
		Method I	Method II
A	—	<0.05	—
B	0.10	0.11	—
	—	—	0.18, 0.17
	0.30	—	0.46

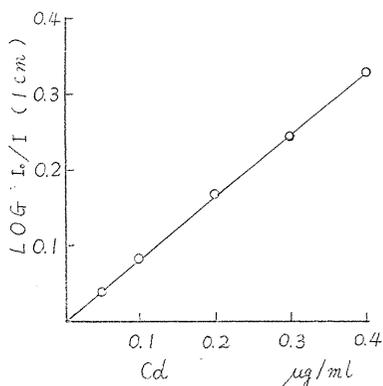


FIG. 5. Determination of cadmium by the dithizone method.

2.1.5. Cobalt

A solution of uranium metal was treated with citric acid and ammonia to adjust pH. Sodium diethyldithiocarbamate solution was added to form the complex of cobalt diethyldithiocarbamate, which was extracted with carbon tetrachloride. Organic phase was evaporated and organic matter in the residue was destroyed with nitric and sulfuric acids. The solution was then adjust pH to 6 with sodium acetate, and nitroso-R salt solution was added. Cobalt nitroso-R complex was produced by heating and then excess of nitroso-R salt was decomposed with hydrochloric acid and hydrogen peroxide. Cobalt was determined by measuring the light absorbance.

PROCEDURE

Sample (1 g):

- Decompose the sample with 10 ml of HCl (6 N),
- Oxidize uranium with H₂O₂ (30%),
- Evaporate the solution to remove excess of HCl,
- Add 10 ml of ammonium citrate solution (15%) to the residue,
- Adjust pH of the solution to 9 with ammonia,
- Transfer the solution to 100 ml separatory funnel and dilute to 25 ml,
- Add 2 ml of freshly prepared sodium diethyldithiocarbamate solution (1%) to the funnel,
- Extract the complex of cobalt with 5 ml of carbon tetrachloride,
- Reserve the organic phase and repeat the extraction procedure three times,

Combined organic phase:

- Evaporate the organic phase on a water bath,
- Decompose the organic matter by treating with each 3 drops of H₂SO₄ and HNO₃,
- Add 5 ml of water and adjust pH to about 6 with sodium acetate,
- Add 0.5 ml of nitroso-R salt solution (0.2%) to it and heat in a water bath for 10 minutes,
- Add 3 ml of HCl (6 N) and 3 drops of H₂O₂ (30%) to the solution and continue heating in a water bath for 30 minutes to decompose excess of nitroso-R salt,

Dilute the solution to 10 (or 15) ml in a volumetric flask,
 Measure the absorbance at 420 m μ ,
 ↓ Run a blank through the procedure and correct the above absorbance.
 Calibration curve is prepared by taking the standard solution and continuing the procedure as described above.

NOTES

1) Excess of nitroso-R salt could be decomposed by heating with 3 ml of HCl (6 N) and 3-5 drops of H₂O₂ (30%) in a water bath for 30 minutes. But the correction was necessary for absorbance because of color of decomposed reagent.

2) Copper (60 ppm) and nickel (100 ppm) extracted as a complex of diethyl-dithiocarbamate had no effect on the determination of cobalt.

3) This method serves to determine more than 0.5 ppm of cobalt.

The calibration curve is shown in Fig. 6.

Results of cobalt obtained by the proposed method and recovery of cobalt added are shown in Table 5.

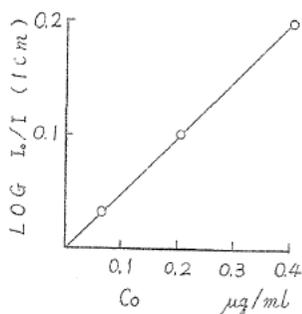


FIG. 6. Determination of cobalt by the nitroso-R salt method.

2.1.6. Copper

A solution of uranium metal was treated with citric acid and ammonia to adjust pH. Disodium ethylenediamine tetraacetate solution and sodium diethyl-dithiocarbamate solution were added to form the complex of copper diethyl-dithiocarbamate, which was then extracted with butyl acetate. Copper was determined by measuring the light absorbance of the extract.

PROCEDURE

Sample (1 g):

Decompose the sample with 10 ml of HCl (6 N),
 Oxidize uranium with H₂O₂ (30%),
 Evaporate the solution to remove excess of HCl,
 Add 10 ml of ammonium citrate solution (15%) to the residue,
 Adjust the pH of the solution to 9 with ammonia,
 Add 1 ml of EDTA solution (4%) to it,
 Transfer the solution to 100 ml separatory funnel and dilute it to 25 ml,
 Add 1.0 ml of freshly prepared sodium diethyldithiocarbamate solution (1%) to the funnel,
 Extract the complex of copper with 5.0 ml of butyl acetate by shaking for 3 minutes,

TABLE 5. Determination of Cobalt by the Proposed Method

Sample	Cobalt added (ppm)	Cobalt found (ppm)
A	—	0.5
	1.1	1.8
B	—	1.1
	1.1	2.1

Organic phase:

Wash the organic phase with 5 ml of H_2SO_4 (2 N) by shaking,
Remove the aqueous phase and filter the organic phase through a dry
filter paper,

Measure the absorbance of the organic phase at 440 m μ ,

↓ Correct the reagent blank.

Calibration curve is prepared by treatment of known amounts of copper as
above.

NOTES

1) It was necessary to wash the organic phase with sulfuric acid for the
determination of trace amounts of copper. Copper diethyldithiocarbamate
complex had no effect in this washing.

2) Nickel and cobalt had no effect because of masking with EDTA.

3) Bismuth (50 μg), silver (25 μg) and lead (50 μg) did not interfere.

4) This method serves to determine 1 to 10 ppm copper.

Typical results obtained for uranium metal are shown in Table 6.

The calibration curve is shown in Fig. 7.

TABLE 6. Determination of Copper by the
Proposed Method

Sample	Copper added (ppm)	Copper found (ppm)
A	—	2.7, 2.5
B	—	10.5, 10.7
	10.5	21.8

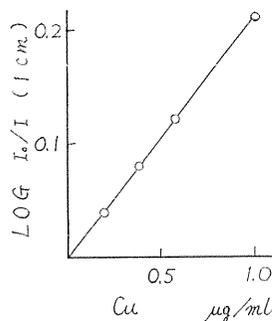


FIG. 7. Determination of copper by
the diethyldithiocarbamate method.

2.1.7. Iron

Method I: A solution of uranium metal was treated with hydroxylamine
hydrochloride to reduce iron and with ammonium acetate to adjust pH to 3.6.
Iron was determined by measuring the absorbance of ferrous-phenanthroline
complex produced by addition of *o*-phenanthroline.

PROCEDURE

Sample (1 g):

Decompose the sample with 4 ml of HCl (1+1),

Oxidize uranium with 0.5 ml of H_2O_2 (30%),

Evaporate the solution almost to dryness on a water bath,

Add 25 ml of water to dissolve the salt,

Reduce iron with 0.5 ml of hydroxylamine hydrochloride solution (10%)
to ferrous state,

Adjust pH of the solution to 3.6 with 10 ml of acetic acid-ammonium
acetate buffer solution (193 g of ammonium acetate and 15 ml of
acetic acid in 1 liter of water),

Transfer the solution to 50 ml of *o*-phenanthroline solution (0.1%),
Dilute the solution to the mark,
↓ Measure the absorbance of the solution at 508 m μ against water.
Calibration curve is prepared by the color development of known amounts of iron as above.

NOTE

This method serves to the determination of more than 10 ppm of iron.

Method II: A solution of uranium metal was treated with sodium thiosulfate to reduce iron and uranium was extracted with TBP-benzene. Ferrous iron in an aqueous phase was oxidized with hydrogen peroxide and bromine, and iron was extracted into TBP-benzene solution followed by the back-extraction into water. Iron was then determined in the same way as in Method I.

PROCEDURE

Sample (0.5 g):

Decompose the sample with 25 ml of HCl (1+1),
Oxidize uranium with 0.5 ml of H₂O₂ (30%),
Boil the solution to decompose excess of peroxide,
Cool the solution and reduce iron to ferrous state by adding 3 ml of sodium thiosulfate solution (2%),
Transfer the solution to 100 ml separatory funnel and remove air in the funnel by introducing a current of carbon dioxide,
Extract uranium by shaking with 25 ml of TBP-benzene solution (30% vol.) for 30 seconds,
Discard the organic phase and repeat this extraction procedure,

Aqueous phase:

Boil the aqueous phase with 1 ml of hydrogen peroxide to oxidize thiosulfate and iron,
Add 3 ml of saturated bromine water to the solution and boil it to oxidize a free sulfur,
Transfer the solution to 100 ml separatory funnel,
Extract iron by shaking with 10 ml of TBP-benzene solution,
Discard the aqueous phase and wash the organic phase by shaking with 3 ml of HCl (1+1),
Back-extract the iron in water,

Aqueous phase:

Add 0.25 ml of hydroxylamine hydrochloride (10%), 2 ml of acetic acid-ammonium acetate solution (2.5 M-1.5 M) and 1 ml of 1, 10 phenanthroline solution (0.1%) to the aqueous phase,

↓ Measure the absorbance of the solution at 508 m μ against water.
Calibration curve is prepared in the same way as in Method I.

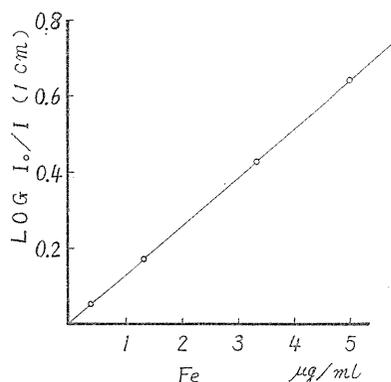
NOTE

This method is suitable for the determination of 2-60 ppm of iron.

The calibration curve obtained by Method I and II is shown in Fig. 8.

Method III: A sample was decomposed with hydrochloric acid and hydrogen peroxide, and the acidity of the solution was adjusted. Iron was then extracted into butyl acetate and determined by color development of iron thiocyanate in

FIG. 8. Determination of iron by the *o*-phenanthroline method.



the organic phase.

PROCEDURE

Sample (0.2 g):

- Decompose the sample with 3 ml of HCl (3+2),
- Oxidize uranium with 0.2 ml of hydrogen peroxide (30%),
- Evaporate the solution to 0.5 to 1 ml,
- Cool and transfer the solution to 50 ml separatory funnel using 10 ml of HCl (3+2),
- Extract iron with 7.0 ml of butyl acetate,

Organic phase:

- Wash the organic phase with 5 ml of HCl (3+2),
- Discard the aqueous phase and repeat the washing of the organic phase with HCl,

Organic phase:

- Dilute the organic phase with methyl isobutylketone to 15 ml,
- Add 5 ml of ammonium thiocyanate solution (20%) to it,
- Shake it for 1 minute and discard the aqueous phase,
- Measure the absorbance at 520 m μ against a mixture of butyl acetate and methyl isobutylketone as a reference solution,

Calibration curve is prepared by treatment of known amounts of iron as above.

NOTES

1) Iron was extracted satisfactorily in hydrochloric acid solution (7 N), but the extractability of iron decreased with increasing acidity.

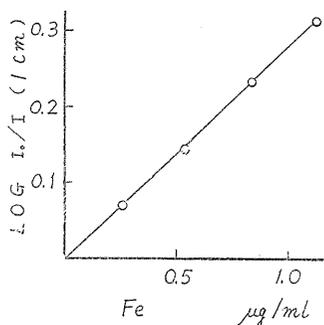


FIG. 9. Determination of iron by the thiocyanate method.

TABLE 7. Determination of Iron by the Proposed Methods

Sample	Iron found (ppm)		
	Method I	Method II	Method III
A	44.6	44.4	—
B	69.1, 68.0	67	—
C	31.9	32.2	—
D	—	—	72, 72, 71
E	—	—	289, 296

2) The slow rise of absorbance with time was observed (absorbance 0.002/10 minutes) for iron thiocyanate color. Therefore, the time for color development must be constant in the range -5 minutes to +5 minutes.

3) This method serves to determine more than 5 ppm of iron.

The calibration curve obtained by Method III is shown in Fig. 9.

The results obtained by three methods are shown in Table 7.

2.1.8. Lead

A solution of uranium metal was treated with ammonium citrate, sodium sulfite and ammonia to adjust pH and to mask other impurities. Lead was extracted as dithizonate with dithizone-benzene solution and determined by measuring the absorbance of the extract.

PROCEDURE

Sample (0.5 to 2.0 g):

- Decompose the sample with 10 ml of HCl (6 N),
- Oxidize uranium with H₂O₂ (30%),
- Evaporate the solution to dryness on a water bath,
- Add 10 ml of HNO₃ (6 N) to the residue to dissolve,
- Transfer the solution to 50 ml separatory funnel,
- Add 4 ml of ammonium citrate solution (50%), 1 ml of sodium sulfite solution (10%) and 4 ml of potassium cyanide solution (2%) to the funnel to mask copper, nickel, iron, zinc etc.,
- Add 3 ml of ammonia to it,
- Extract the complex of lead dithizonate with 5 ml of dithizone-benzene solution (0.005%) by shaking for about 2 minutes,

Organic phase:

- Wash it with mixed solution (10 ml of water, 0.5 ml of sodium sulfite solution (10%), and 0.5 ml of potassium cyanide solution (2%)) by shaking for about 1 minute,
- Reject the aqueous phase and re-wash the organic phase with 10 ml of sodium sulfite solution (0.5%) by shaking,
- Measure the absorbance of the organic phase at 520 m μ against benzene,
- ↓ Correct the reagent blank.

Calibration curve is prepared by treatment of known amounts of lead as above.

NOTES

- 1) This method serves to determine more than 1 ppm of lead.
- 2) Care must be taken of lest the positive error should be produced by the oxidation of dithizone.
- 3) Benzene was superior to other solvents for extraction of lead in standpoint of simplicity of extraction and washing of extract.

The results obtained by the proposed method are shown in Table 8.

The calibration curve is shown in Fig. 10.

2.1.9. Manganese

A sample was dissolved and uranium was separated by extracting with TBP-carbon tetrachloride. Manganese remaining in the aqueous phase was determined

TABLE 8. Determination of Lead by the Proposed Method

Sample	Lead added (ppm)	Lead found (ppm)
A	—	4.0, 4.4, 4.2
B	—	3.8
C	2.0	5.8

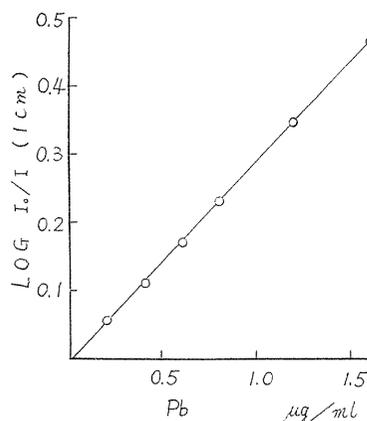


FIG. 10. Determination of lead by the dithizone method.

photometrically to measure the permanganic acid obtained by oxidation of manganese (II).

PROCEDURE

Sample (2 g):

- Decompose the sample with 7 ml of HCl (1+2),
- Oxidize uranium with 10 ml of HNO₃,
- Evaporate the solution to about 5 ml,
- Cool and add 10 ml of water to the residue,
- Transfer the solution to 50 ml separatory funnel,
- Extract uranium by shaking with 10 ml of TBP-carbon tetrachloride solution (3+7) for 30 seconds,
- Reject the organic phase, and repeat the extraction of uranium with 10 ml of TBP-carbon tetrachloride two times,
- Remove the remaining TBP in the aqueous phase by shaking with 10 ml of carbon tetrachloride,

Aqueous phase:

- Transfer the aqueous phase to 50 ml Erlenmeyer flask,
- Add 1 ml of H₂SO₄ (1+1) to the flask,
- Evaporate it until fumes of sulfuric acid are evolved,
- Add 1 ml of HNO₃ to the residue and repeat the evaporation,
- Cool and add 7 ml of water to the residue,
- Add 0.5 ml of silver nitrate solution (1%) and 1 ml of ammonium persulfate solution (20%) to it,
- Boil it for 1 minute to oxidize manganese to permanganate,
- Cool and dilute it to 10 ml,

↓ Measure the absorbance of the solution at 525 or 545 mμ against water.

Calibration curve is prepared by measuring an absorbance of permanganate solution.

NOTES

- 1) Potassium periodate can be used in place of ammonium persulfate.

2) Two to 80 ppm of manganese can be determined conveniently by this method.

3) If the colored ions are present in the sample solution, the remaining portion of the solution is decolorized by treatment with urea and sodium nitrite solution and the absorbance of this solution is measured for subtracting from the sample absorbance.

The results obtained for typical samples are shown in Table 9.

The calibration curve is shown in Fig. 11.

TABLE 9. Determination of Manganese by the Proposed Method

Sample	Manganese found (ppm)
A	4.7, 4.7, 4.7
B	5.6, 5.3, 5.5

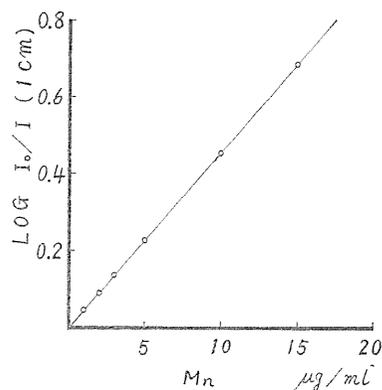


FIG. 11. Determination of manganese by the permanganate method.

2.1.10. Molybdenum

A sample was dissolved and the acidity of the solution was adjusted. Molybdenum was extracted with butyl acetate, and treated with a solution containing ammonium thiocyanate, stannous chloride and perchloric acid to develop the color of molybdenum thiocyanate.

PROCEDURE

Sample (1 g):

- Decompose the sample with 5 ml of HCl (1+1),
- Oxidize uranium with 1 ml of H₂O₂ (30%),
- Boil the solution to decompose peroxide and evaporate to 1-2 ml,
- Add 18 ml of HCl (1+1) to it,
- Transfer the solution to 50 ml separatory funnel,
- Extract molybdenum by shaking with 9 ml of butyl acetate for 1 minute,
- Reserve the organic phase and repeat the extraction of molybdenum with 5 ml of butyl acetate from the aqueous phase,
- Discard the aqueous phase and combine the organic phase,

Combined organic phase:

- Wash the organic phase with 5 ml of HCl (1+1) two times, and discard the aqueous phase,
- Add 3 ml of ammonium thiocyanate solution (22.8 g/100 ml) to it,
- Shake it for 10 seconds and add to 0.2-0.3 ml of stannous chloride solution (10%),
- Shake it again for 30 minutes,
- Add 2 ml of perchloric acid (15%) to it and shake for 1 minute,

Discard the aqueous phase,
 Add 10 ml of HCl (3+5) to the organic phase and repeat the above procedure for coloration,
 Discard the aqueous phase, and transfer the organic phase to 15 ml volumetric flask,
 Dilute it with butyl acetate,
 Centrifuge it to remove water droplets,
 ↓ Measure the absorbance at 460 m μ against butyl acetate.
 Calibration curve is prepared by treatment of known amounts of molybdenum and 20–30 μ g of iron as above.

NOTES

1) Care must be taken of regulating the amount of iron to less than 300 μ g. If more than 300 μ g of iron is present, the coloration procedure of molybdenum must be repeated three times.

2) Because of promotion effect of iron for molybdenum thiocyanate coloration, a small amount of iron is used for preparation of calibration curve.

3) This method serves to determine 1–200 ppm of molybdenum.

The results obtained for molybdenum and recovery of molybdenum added to uranium sample are shown in Table 10, and the calibration curve is shown in Fig. 12.

TABLE 10. Determination of Molybdenum by the Proposed Method

Sample	Molybdenum added (ppm)	Molybdenum found (ppm)
A	—	0.1
	4.0	4.3
	10.0	10.0
B	—	0.5
	4.0	4.7

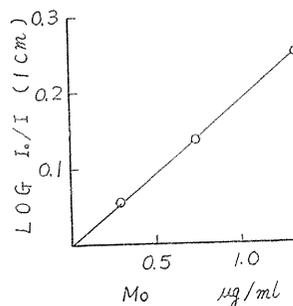


FIG. 12. Determination of molybdenum by the thiocyanate method.

2.1.11. Nickel

A solution of uranium metal was treated with citrate and ammonia to adjust pH. Nickel was extracted as nickel dimethylglyoximate complex with chloroform and was determined photometrically.

PROCEDURE

Sample (1 g):

Decompose the sample with 10 ml of HCl (6 N),
 Oxidize uranium with H₂O₂ (30%),
 Evaporate the solution to remove excess of HCl,
 Add 10 ml of ammonium citrate solution (15%) to the residue,
 Adjust pH of the solution to 9 with ammonia,
 Transfer the solution to 100 ml separatory funnel and dilute to 30 ml,

Add 2 ml of freshly prepared sodium dimethylglyoxime solution (0.5%) to the funnel,

Extract the complex of nickel dimethylglyoximate with 10 ml of chloroform by shaking for 1 minute,

Organic phase:

Transfer another separatory funnel containing hydroxylamine-ammonium citrate solution (0.25% in hydroxylamine hydrochloride and 15% in ammonium citrate, pH of this solution 9),

Shake it for 1 minute,

Filter the organic phase through a dry filter paper,

Measure the absorbance of the organic phase at $375\text{ m}\mu$ against chloroform,

Correct the reagent blank.

Calibration curve is prepared by treatment of known amounts of nickel as above.

NOTES

1) Optimum pH range for extraction of nickel dimethylglyoximate was 8.6 to 9.8.

2) This method is carried out conveniently by regulating the nickel content to 5-50 μg .

The results obtained by the proposed method are shown in Table 11 and the calibration curve is shown in Fig. 13.

TABLE 11. Determination of Nickel by the Proposed Method

Sample	Nickel added (ppm)	Copper added (ppm)	Nickel found (ppm)
A	—	—	5.6
	5	—	11.6
B	—	—	19.5
	—	1000	19.5

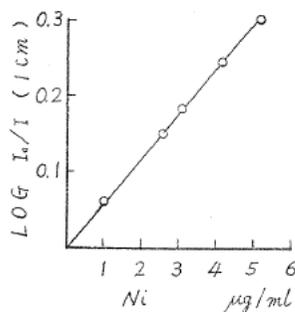


FIG. 13. Determination of nickel by the dimethylglyoximate-extraction method.

2.1.12. Nitrogen

A sample was dissolved in hydrochloric acid and nitrogen was distilled from an alkaline solution in the steam distillation unit. Ammonia in the distillate was then determined photometrically with a pyridine-pyrazolone method.

PROCEDURE

Sample (0.2 g):

Place the sample in the distillation flask (Fig. 14),

Add 10 ml of HCl (1+1) to the flask,

Heat it gently to decompose,

Cool and connect the still (receiving separatory funnel contains a water),

Add 30 ml of NaOH (50%) through the funnel (b) to the flask,
Distill ammonia by allowing steam from the generator to enter the distillation flask,

Lower the receiving funnel so that the delivery tip may be above the level of the solution when 15 ml of distillate is collected,

Repeat the distillation until 20 ml of distillate is collected,

Distillate:

Add 10 ml of acetic acid-sodium acetate buffer solution (pH 3.7) and 1 ml of Chloramine-T (3%) to the distillate,

Shake it and stand for 2 minutes,

Add 20 ml of pyrazolone solution (0.25%) and 4 ml of bis-pyrazolone-pyridine solution (0.1%; this solution is prepared just prior to the time it is mixed with the aqueous pyrazolone solution) to the solution,

Extract ammonia color with 20 ml of carbon tetrachloride after 1 minute,

Filter the extract through a dry filter paper to remove water droplets,

Measure the absorbance of the extract,

Correct for blank.

Calibration curve is prepared by treatment of known amounts of ammonium chloride as above except distillation.

NOTES

1) Borosilicate distillation apparatus was suitable for this manipulation.

2) This method serves to determine more than 5 ppm of nitrogen.

Distillation apparatus is shown in Fig. 14 and the calibration curve of nitrogen is shown in Fig. 15.

The results obtained for typical sample are shown in Table 12.

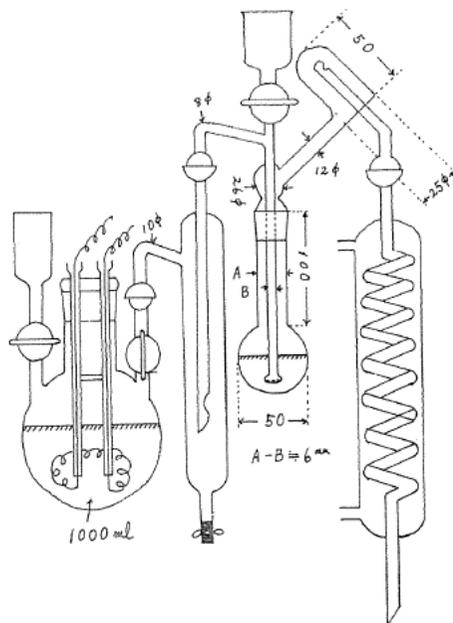


FIG. 14. Distillation apparatus for the determination of nitrogen.

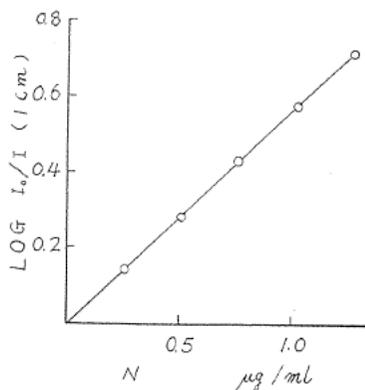


FIG. 15. Determination of nitrogen by the pyridine-pyrazolone method.

TABLE 12. Determination of Nitrogen by the Proposed Method

Sample	Nitrogen found (ppm)
A	36, 38, 38
B	60, 62, 63
C	36, 34, 34

2.1.13. Phosphorus

A sample was decomposed with nitric and perchloric acids, and arsenic in this solution was volatilized by evaporating with sodium bromide until fumes of perchloric acid are evolved. Phosphorus was then extracted as molybdophosphoric acid which reduced to heteropoly blue.

PROCEDURE

Sample (0.5 g):

- Decompose the sample with 5 ml of HNO_3 ,
- Add 6 ml of HClO_4 (60%) to it,
- Evaporate the solution and fume for 2 minutes,
- Cool and add 3 ml of sodium bromide solution (30%) to the residue,
- Evaporate and fume it for 3 minutes to remove the bromide,
- Cool and add 3 ml of ammonium molybdate solution (10%) to it,
- Stir and stand it for 5 minutes,
- Transfer the solution to 100 ml separatory funnel,
- Extract the molybdophosphoric acid by shaking with 10 ml of methyl isobutylketone,
- Transfer the aqueous phase to another separatory funnel and repeat the extraction with 5 ml of methyl isobutylketone,

Combined organic phase:

- Wash the organic phase with 10 ml of HCl (0.5 N) two times,
- Transfer the organic phase to 20 ml volumetric flask,
- Add 4 ml of ethanol (99%) and 0.15 ml of stannous chloride solution (50%) to it, and dilute it with ethanol (99%) to the mark,
- Shake and stand it for 15 minutes,
- Measure the absorbance of the solution at 725 or 625 $\text{m}\mu$ against a mixture of methyl isobutylketone and ethanol (3+1) as a reference.

Calibration curve is prepared by treatment of known amounts of phosphorus as above except arsenic volatilization with sodium bromide.

NOTE

This procedure serves to determine more than 2 ppm of phosphorus.

The results obtained by the proposed method are shown in Table 13.

The calibration curve is shown in Fig. 16.

TABLE 13. Determination of Phosphorus by the Proposed Method

Sample	Phosphorus added (ppm)	Phosphorus found (ppm)
A	—	8.5, 8.3, 8.3
	2.0	10.5
B	—	10.6, 11.0, 10.9
	10.0	21.4

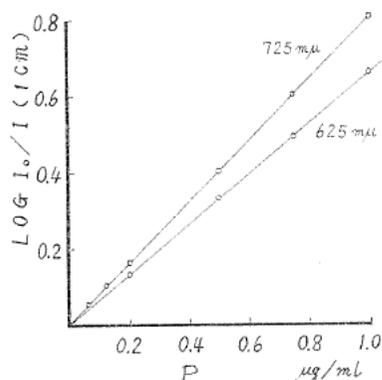


FIG. 16. Determination of phosphorus by the molybdenum blue method.

2.1.14. Silicon

A sample was decomposed with hydrochloric acid and hydrogen peroxide (acid-soluble silicon). Silicon in a solution of the sample was determined by extraction of molybdosilicic acid and reduction to heteropoly blue. In the determination of total silicon, the sample was decomposed with nitric acid followed by fusion with carbonate.

PROCEDURE

(a) Acid-soluble silicon

Sample (0.2 g):

- Place the sample in a polyethylene beaker,
- Decompose the sample with 2.2 ml of H_2O_2 (3%) and 2.3 ml of HCl (1+1),
- Heat the beaker on a water bath if necessary,
- Add 10 ml of water to the beaker,
- Add potassium permanganate solution (1%) dropwise to give the solution a pink color to decompose excess of peroxide,
- Dilute the solution to 25 ml,
- Add 5 ml of ammonium molybdate solution (10%) to the solution,
- Stir and stand it for 5 minutes,
- Add 5 ml of oxalic acid solution (10%) to it,
- Transfer the solution to 50 ml separatory funnel,
- Extract the molybdosilicic acid by shaking with 15 ml of methyl isobutyl-ketone for 1 minute,
- Discard the aqueous phase and wash the organic phase by shaking with 5 ml of HCl (0.5 N) two times,

Organic phase:

- Transfer the organic phase to 20 ml volumetric flask,
 Add 4 ml of ethanol (99%) and 0.15 ml of stannous chloride solution (50%)
 to the flask,
 Dilute it with ethanol to the mark,
 Measure the absorbance of the solution at 770 (or 630) $m\mu$ against a
 mixture of methyl isobutylketone and ethanol (3+1) as a reference
 solution after allowing it to stand for 15 minutes,
 ↓
 Calibration curve is prepared by treatment of known amounts of silicon as
 above.

NOTE

Molybdosilicic acid was effectively extracted from 0.2-0.5 N hydrochloric acid solution.

(b) Total silicon

Sample (0.2 g):

- Place the sample in a platinum crucible,
 Add 2 ml of HNO_3 to the crucible,
 Cover and heat it gently to decompose,
 Wash away the cover with a jet of water,
 Evaporate the solution to dryness,
 Add 10 ml of water to dissolve the uranyl salt,
 Add 1.0 g of sodium carbonate to the solution,
 Stir it to complete solution as uranyl carbonate complex,
 Evaporate to dryness and fuse it,
 Cool and add 15 ml of water to the melt,
 Leach the melt with 15 ml of water,
 Transfer it to polyethylene beaker,
 Add 5.2 ml of HCl (1+1) to the beaker,
 Dilute it with water to 25 ml,
 Add 5 ml of ammonium molybdate solution (10%) to the solution and
 ↓ allow it to stand for 5 minutes,
 Proceed in the same manner as acid-soluble silicon.

NOTES

- 1) Reagents used must be free from silicon.

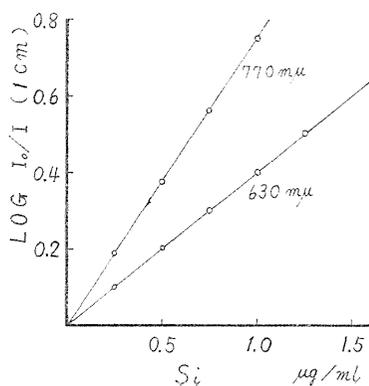


FIG. 17. Determination of silicon by the molybdenum blue method.

TABLE 14. Determination of Acid-soluble and Total Silicon

Sample	Acid-soluble silicon (ppm)	Total silicon (ppm)
A	49.4, 47.6, 48.1	55.3, 54.8, 54.6
B	44.4, 45.7	65.0, 61.8, 62.3

2) Silicon may be determined by this method when present in amounts between 5–150 ppm in amount.

The calibration curves are shown in Fig. 17.

Results obtained by the proposed method are shown in Table 14.

2.1.15. Silver

A sample was decomposed with nitric and sulfuric acids, and silver in this solution was separated by co-precipitation with thallium iodide. After decomposing the precipitate, the silver was determined photomerically as silver-dimethylaminobenzylidenerhodanate.

PROCEDURE

Sample (5 g):

Decompose the sample with 20 ml of HNO_3 ,

Add 30 ml of H_2SO_4 (1+1) to it,

Evaporate it until fumes of sulfuric acid are evolved,

Cool and add 200 ml of water to it.

Add 2 ml of thallosulfate solution (1%) and 5 ml of potassium iodide solution (5%) to it,

Mix, filter the precipitate on a small filter paper and wash with water,

Thallosulfate precipitate containing silver:

Transfer the precipitate to 100 ml beaker by directing a jet of hot water, and transfer the remaining precipitate on to the filter paper by dissolving in hot sulfuric acid-hydrogen peroxide solution (1 ml of H_2SO_4 (1+1) and 1 ml of hydrogen peroxide (30%) are added to 30 ml of water and this solution is heat for boiling),

Heat it to dissolve the thallosulfate precipitate,

Boil the solution to expel iodine,

Evaporate the solution until fumes of sulfuric acid are evolved,

Cool and add 3 ml of acetic acid-ammonium acetate solution (8 g of ammonium acetate is dissolved in 33 ml of acetic acid and 67 ml of water) to it to dissolve the thallosulfate,

Add 2 ml of dimethylaminobenzylidenerhodanine solution (0.01%) to it,

Measure the absorbance of the solution against acetic acid-ammonium acetate and dimethylaminobenzylidenerhodanine-acetic acid mixed solution as a reference solution.

↓
Calibration curve is prepared by treatment of 2 ml of known amounts of silver with 1 ml of acetic acid and 2 ml of dimethylaminobenzylidenerhodanine solution.

NOTE

This method serves to determine 0.4–4 ppm of silver.

The results obtained for silver in uranium metal and recovery of silver added in uranium sample are shown in Table 15.

The calibration curve is shown in Fig. 18.

TABLE 15. Determination of Silver by the Proposed Method

Sample	Silver added (ppm)	Silver found (ppm)
A	—	<0.4 (about 0.2)
	0.5	0.6
	1.0	1.2
B	—	<0.4
	2.0	2.1

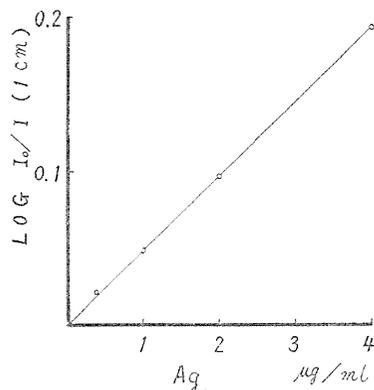


FIG. 18. Determination of silver by the dimethylaminobenzylidenerhodanine method.

2.1.16. Thorium

A solution of uranium metal was treated with TBP-benzene solution to remove uranium, and thorium remained in an aqueous phase was determined photometrically as thorium thordin complex.

PROCEDURE

Sample (1 g):

Decompose the sample with 50 ml of HCl (5 N),
Oxidize uranium with 1.5 ml of H₂O₂ (30%),
(If the insoluble residue remains, fuse the residue with sodium carbonate.)

Transfer the solution to 150 ml separatory funnel,
Adjust the acidity of HCl to 4.5-5 N,
Extract uranium by shaking with 50 ml of TBP-benzene solution (3+7),
Reject the organic phase and repeat the extraction until no color is observed on the organic phase,

Aqueous phase:

Wash the aqueous phase with 10 ml of benzene by shaking to remove remaining TBP,

Evaporate it to dryness on a water bath,

Add 1.0 ml of HCl (1+9) to dissolve the residue,

Add 4 ml of water and boil it for complete dissolution of the residue,

Cool and transfer the solution to 10 ml volumetric flask,

Add water to about 7 ml,

Add 2.0 ml of thordin solution (0.02%) and dilute it to the mark,

Measure the absorbance of the solution at 545 m μ against a mixture of thordin solution and hydrochloric acid as a reference solution.

Calibration curve is prepared by direct color development of known amounts of thorium.

NOTES

- 1) This method is suitable for the determination of 10–60 ppm of thorium.
- 2) Thorium does not be extracted in 4.5–5 N hydrochloric acid solution.

The results obtained for typical samples are shown in Table 16.

The calibration curve is shown in Fig. 19.

TABLE 16. Determination of Thorium by the Proposed Method

Sample	Thorium found (ppm)		
	Proposed method	Ion exchange method	
A	554, 550, 564	551, 538, 560	
B	1030, 1030, 1060	983, 999, 991	
C	731, 793, 725	720, 700, 710	

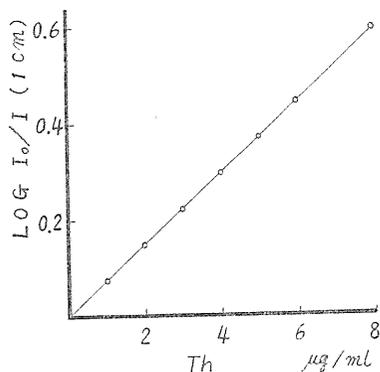


FIG. 19. Determination of thorium by the thoring method.

2.1.17. Zirconium

A sample was decomposed and zirconium was separated from uranium by extraction with TBP. Zirconium in an aqueous phase was determined photometrically as zirconium alizaline-sulfonate complex after treatment of aqueous phase with perchloric acid.

PROCEDURE

Sample (1 g):

- Decompose the sample with 5 ml of HCl (1+1),
- Oxidize uranium with H₂O₂ (30%),
- Add 3 ml of HClO₄ (60%) and 0.5 ml of hydrofluoric acid (45%) to the solution,
- Evaporate the solution until fumes of HClO₄ are evolved,
- Cool and add 10 ml of HCl (4.5 N) to dissolve the salt,
- Transfer the solution to 100 ml separatory funnel,
- Extract uranium by shaking with 15 ml of TBP-benzene solution (3+7) three times,

Aqueous phase:

- Add 10 ml of HCl (12 N) and 20 ml of TBP-benzene solution (3+7) to the aqueous phase,
- Extract zirconium by shaking for 1 minute,
- Reserve the organic phase and repeat the extraction procedure two times,

Combined organic phase:

- Back-extract zirconium into 10 ml of water,

Aqueous phase:

Wash the aqueous phase with 10 ml of benzene by shaking,
 Discard the organic phase,
 Add 1.0 ml of HClO_4 (60%) to the aqueous phase,
 Evaporate the solution until fumes of HClO_4 are evolved,
 Cool and add 8 ml of water and 1.00 ml of sodium alizarine-sulfonate solution (0.15%) to it,
 Boil the solution for 1 minute,
 Cool, transfer the solution to 10 ml volumetric flask and dilute to the mark,
 Measure the absorbance of the solution at $525 \text{ m}\mu$ against a mixture of perchloric acid, water and sodium alizaline-sulfonate solution as a reference solution.

↓
 Calibration curve is prepared by treatment of known amounts of zirconium as above after evaporation with 1.0 ml of HClO_4 (60%).

NOTES

- 1) Phosphate must be absent. In this method, phosphorus can be removed as phosphine in decomposition of the sample with hydrochloric acid.
- 2) This method is suitable for the determination of 5 to 100 ppm of zirconium.
- 3) The effect of less than 0.3 mg of sulfate per 10 ml is negligible.

The results obtained for various sample of uranium metal are shown in Table 17.

The calibration curves are shown in Fig. 20.

TABLE 17. Determination of Zirconium by the Proposed Method

Sample	Zirconium added (ppm)	Zirconium found (ppm)
A	—	54.3, 55.4, 53.2
	10.0	64.8
B	—	<5, <5, <5
	20.0	20.8

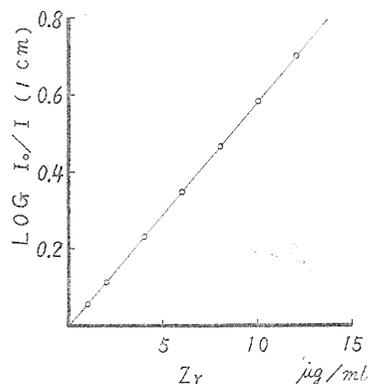


FIG. 20. Determination of zirconium by the alizarine-sulfonate method.

2.2. Polarographic method

2.2.1. Apparatus

Yanagimoto pen-recording polarograph PA-101 was used and A. C. polarogram was measured through this study. Span voltage was 1 V for recording. Samples were deaerated using prepurified nitrogen and held at 25° in a water thermostat.

2.2.2. Cadmium

A sample was decomposed in hydrochloric acid and hydrogen peroxide, and then cadmium was separated by extraction as an iodo-complex. Cadmium was determined by A. C. polarography after back-extraction into water.

PROCEDURE

Sample (5 g):

- Decompose the sample with 20 ml of HCl (1+1),
- Oxidize uranium with 5 ml of H₂O₂ (30%),
- Evaporate the solution almost to dryness,
- Add 15 ml of water to the salt to dissolve,
- Add 1 ml of hydroxylamine hydrochloride solution (10%) to it,
- Add 10 ml of potassium iodide solution (3 M), 25 ml of trisodium citrate solution (50%) and 3 ml of sodium thiosulfate solution (1 M) to it,
- Adjust pH of the solution to 6-8 with ammonia,
- Transfer the solution to 100 ml separatory funnel,
- Extract the iodo-complex of cadmium by shaking with 25 ml of methyl isobutylketone for 1 minute,
- Reserve the organic phase and repeat the extraction two times,

Combined organic phase:

- Back-extract cadmium into 10 ml of water,

Aqueous phase:

- Transfer the aqueous phase to 50 ml quartz evaporating dish,
- Evaporate it to dryness,
- Add exactly 1 ml of HClO₄ (1+9) to the residue,
- Transfer the solution to a polarographic cell,
- Scanning from -0.8 to -1.1 volt vs. mercury pool at 25°,
- Measure the wave height of cadmium at -0.92 volt.

Calibration curve is prepared with cadmium standard solution using perchloric acid (1+9) as a supporting electrolyte.

NOTE

This method is suitable for the determination of more than 0.02 ppm of

TABLE 18. Determination of Cadmium by the Proposed Method

Sample	Cadmium added (ppm)	Cadmium found (ppm)
A	—	0.00
	0.200	0.201, 0.207, 0.208
B	—	0.17, 0.17, 0.18

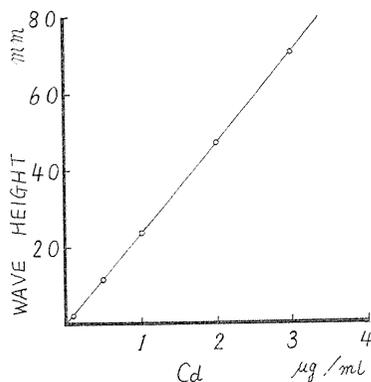


FIG. 21. Determination of cadmium by the polarographic method.

cadmium.

The results obtained for typical samples are shown in Table 18 and the calibration curve is shown in Fig. 21.

2.2.3. Chlorine

A sample was decomposed with sulfuric acid and hydrogen peroxide, and chloride was determined by A. C. polarography.

PROCEDURE

Sample (1 g):

- Place the sample in a 50 ml Erlenmeyer flask fitted with reflux condenser,
- Add 5 ml of hydrogen peroxide (30%) and 1.5 ml of sulfuric acid to the flask,
- Heat gently the sample to decompose,
- Boil the solution to decompose the excess of peroxide,
- Cool and add 1.0 ml of sulfuric acid to it,
- Transfer the solution to 10 ml volumetric flask and dilute to the mark,
- Transfer the solution to a polarographic cell,
- Scanning from -0.05 to -0.25 volt vs. mercury pool at 25° ,
- ↓ Measure the wave height of chloride ion at -0.15 volt,

Calibration curve is prepared as follows: Uranium trioxide containing no chlorine is dissolved in H_2SO_4 and treated as the above procedure with known amounts of chloride ion.

NOTES

1) This method is owing to measuring oxidation wave of mercury in the presence of chloride ion. $2Hg + 2Cl^- = Hg_2Cl_2 + 2e$

2) The sample solution must not contact with anode mercury pool before measuring polarogram. It is desired to use the external half cell.

3) This method serves to determine more than 1 ppm of chlorine.

The results obtained for typical samples are shown in Table 19.

A. C. polarogram is shown in Fig. 22 and calibration curve in Fig. 23.

TABLE 19. Determination of Chlorine by the Proposed Method

Chlorine added (ppm)	Chlorine found (ppm)
—	2.6, 2.4
20.0	23.2
24.0 (+Br 200 ppm)	26.6

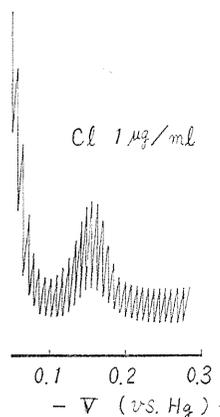


FIG. 22. A. C. polarogram of chlorine.

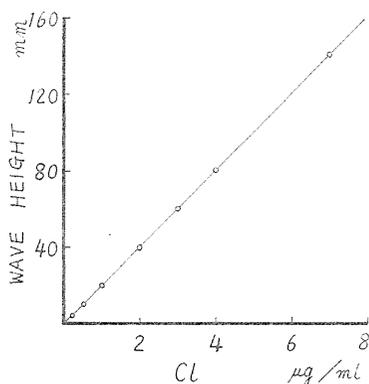


FIG. 23. Determination of chlorine by the polarographic method.

2.2.4. Lead

A solution of uranium metal was treated with ammonium citrate, sodium sulfite and ammonia to mask the other trace impurities. Lead was extracted as dithizonate with dithizone-benzene solution and then lead was back-extracted into dilute perchloric acid. Lead in perchloric acid solution was determined by A. C. polarography.

PROCEDURE

Sample (0.5-2.0 g):

↓ Tread the sample as described in 2.1.8,

Organic phase (containing lead dithizonate):

↓ Back-extract the lead by shaking with 2.0 ml of perchloric acid solution (1+19),

Aqueous phase:

↓ Transfer the aqueous phase to a polarographic cell and remove dissolved oxygen by introducing nitrogen into the solution,

Scanning from -0.5 to -0.9 volt vs. mercury pool electrode,

↓ Measure the wave height of lead at -0.72 volt,

Calibration curve is prepared with the standard solution as above using supporting electrolyte of perchloric acid (1+19).

TABLE 20. Determination of Lead by the Proposed Method

Sample	Lead found (ppm)	
	Proposed method	Photometric method
A	3.8, 4.0, 4.0	4.2
B	4.6, 4.8, 4.8	5.0

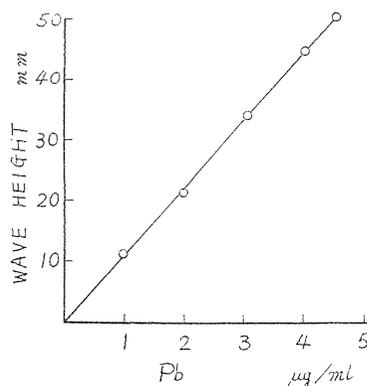


FIG. 24. Determination of lead by the polarographic method.

NOTES

1) A. C. polarographic measurement of trace amounts of lead was made satisfactorily in dilute perchloric acid medium (0.45 N).

2) This method is suitable for the determination of more than 1 ppm of lead.

The results obtained by the proposed method are compared with those by photometric method in Table 20.

Calibration curve is shown in Fig. 24.

2.2.5. Simultaneous determination of copper, lead, cadmium, zinc, nickel and cobalt (dithizone extraction-A. C. polarography)

A sample solution of uranium metal was treated with ammonium citrate, and ammonia to adjust pH to 8.5-9.0, and copper, lead, cadmium, zinc, nickel and cobalt were extracted as dithizonates with dithizone-benzene solution. Lead, cadmium and zinc were back-extracted into perchloric acid solution, and the former two metals were determined by A. C. polarography. Zinc was determined polarographically after addition of pyridine to this solution. On the other hand, the organic phase was heated almost to dryness to expel benzene and the residue was heated with perchloric acid to decompose the organic matter. Nickel and cobalt were determined by A. C. polarography after addition of pyridine.

PROCEDURE

Sample (2.0 g):

Decompose the sample with HCl (6 N),
 Oxidize uranium with H₂O₂ (30%),
 Evaporate the solution to dryness on a water bath,
 Dissolve the residue in HCl (1+100),
 Transfer the solution to 50 ml separatory funnel,
 Add 5 ml of ammonium citrate (50%) to the funnel,
 Adjust pH to about 9 with ammonia,
 Extract it with 10 ml of dithizone-benzene solution (0.005%),
 Reserve the organic phase and repeat the extraction with 10 ml portion of dithizone solution,

Combined organic phase:

Wash the organic phase with ammonia (1+100) and then with water,
 Back-extract lead, cadmium and zinc by shaking with 2.00 ml of perchloric acid (0.3 N),

Aqueous phase:

Transfer the aqueous phase to a polarographic cell and remove dissolved oxygen by introducing nitrogen into the solution,
 Scanning from -0.50 to -0.90 volt vs. mercury pool electrode,
 Measure the wave height of cop-

Organic phase:

Transfer the organic phase to a quartz beaker,
 Evaporate it to dryness on a sand bath,
 Add 3 ml of perchloric acid (60%) to the residue,
 Fume it to decompose the organic matter,
 Dissolve the residue in 2.00 ml

per at -0.20 volt, lead at -0.60 volt and cadmium at -0.80 volt,
 Add 0.20 ml of pyridine to polarographic cell,
 Scanning from -1.05 to -1.25 volt vs. mercury pool electrode,
 Measure the wave height of zinc at -1.16 volt.

of perchloric acid (0.3 N),
 Scanning from -0.10 to -0.30 volt vs. mercury pool electrode,
 Measure the wave height of copper at -0.20 volt,
 Put 0.20 ml of pyridine into polarographic cell,
 Scanning from -0.80 to -1.10 volt vs. mercury pool electrode,
 Measure the wave height of nickel at -0.95 volt and cobalt at -1.18 volt.

Calibration curves are prepared with the standard solution using perchloric acid (0.3 N) as a supporting electrolyte for copper, lead and cadmium and perchloric acid (0.3 N) 2.0 ml + pyridine 0.2 ml for zinc, nickel and cobalt.

NOTE

This method serves to determine more than 0.15 ppm of cadmium, 0.2 ppm of copper, 0.2 ppm of lead, 0.25 ppm of zinc, 0.25 ppm of cobalt and 0.4 ppm of nickel.

The results obtained by the proposed method are shown in Table 21.

Calibration curves are shown in Fig. 25 for cadmium, copper, lead, zinc, cobalt and nickel.

TABLE 21. Determination of Copper, Lead, Cadmium, Zinc, Nickel and Cobalt

Sample	Found (ppm)					
	Copper	Lead	Cadmium	Zinc	Nickel	Cobalt
A	2.5, 2.6	1.1, 1.1	<0.2, <0.2	4.1, 4.1	75, 73	<0.3, <0.3
B	1.9	1.1	<0.2	4.2	47	<0.3
C	0.8	0.3	0.2	1.5	1.5	0.3

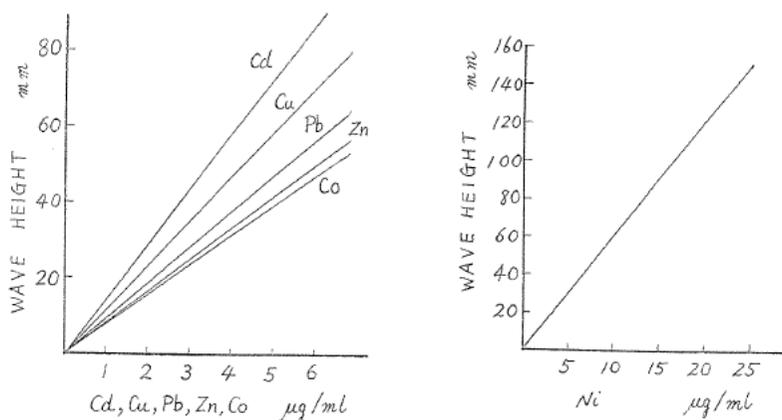


FIG. 25. Determination of cadmium, copper, lead, zinc, cobalt and nickel by the polarographic method.

2.2.6. Simultaneous determination of cadmium, cobalt, copper, iron, manganese, nickel, lead and zinc

A sample was dissolved and uranium was removed by extraction with TBP. Copper, lead, cadmium and zinc were determined by A. C. polarography using perchloric acid-hydrochloric acid-tartaric acid solution as a supporting electrolyte, and cadmium, nickel, cobalt, zinc and manganese were determined by A. C. polarography after addition of ammonia to the above supporting electrolyte.

PROCEDURE

Sample (2 g):

Decompose the sample with 20 ml of HNO_3 ,
Evaporate the solution to about 10 ml,
Cool it by adding 10 ml of water,
Transfer the solution to 100 ml separatory funnel,
Extract uranium by shaking with 20 ml of TBP-carbon tetrachloride (3+7),
Reject the organic phase and repeat the extraction of uranium with TBP-carbon tetrachloride,

Aqueous phase:

Remove the remaining TBP by shaking with 10 ml of carbon tetrachloride,
Draw off the organic phase and transfer the aqueous phase into 50 ml quartz dish,
Add 2 ml of perchloric acid (60%) to it,
Evaporate the solution to dryness on a sand bath to decompose the organic matter,
Cool and add 2 ml of perchloric acid-hydrochloric acid-tartaric acid mixture (80 ml of HClO_4 (60%), 1 ml of HCl and 1.5 g of tartaric acid in 1 liter of water) to the residue,
Transfer the solution to a polarographic cell and remove the dissolved oxygen by introducing nitrogen into the solution,
Scanning from -0.05 to -1.30 volt vs. mercury pool electrode at 25°C ,
Measure the wave height of copper at -0.18 volt, lead at -0.60 volt, cadmium at -0.80 volt and zinc at -1.18 volt,
Add 0.4 ml of ammonia (10 M) to the solution in the cell and remove the dissolved oxygen,
Scanning from -0.50 to -1.70 volt vs. mercury pool electrode,
Measure the wave height of cadmium at -0.70 volt, nickel at -0.98 volt, cobalt at -1.18 volt, zinc at -1.25 volt, iron at -1.38 volt and manganese at -1.75 volt.

Calibration curves are prepared by measuring the wave height produced by treatment of known amounts of metals using the same supporting electrolyte as above.

NOTE

This method serves to the simultaneous determination of 0.1-15 ppm of cadmium, 0.5-40 ppm of cobalt, 0.2-20 ppm of copper, 0.5-40 ppm of iron, 1-30 ppm of manganese, 0.5-40 ppm of nickel, 0.2-20 ppm of lead and 0.3-30 ppm of zinc.

A. C. polarograms obtained are shown in Fig. 26 and calibration curves are

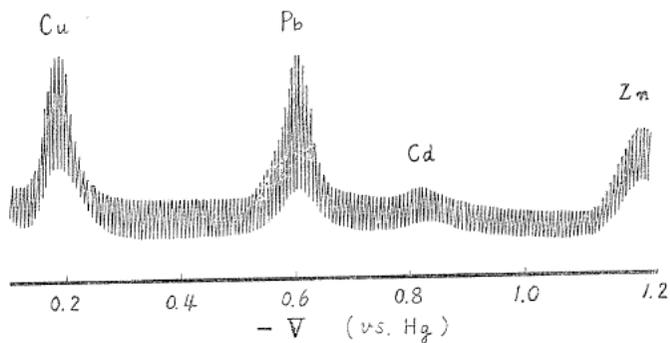


FIG. 26-1. A. C. polarogram of copper, lead, cadmium and zinc
Supporting electrolyte, HClO_4 0.5 M-HCl 0.001 M-tartaric acid 0.01 M.

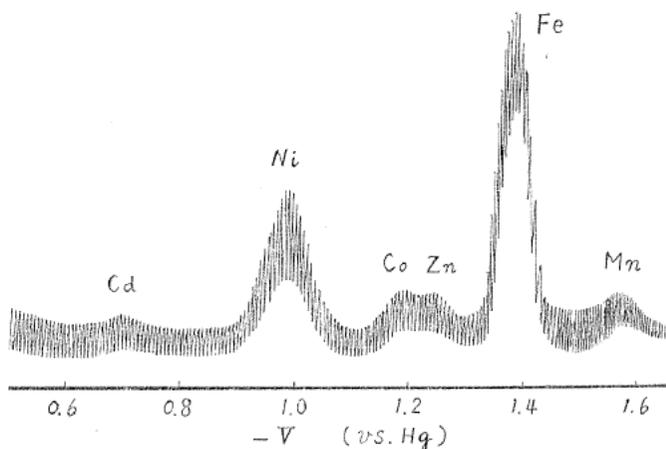


FIG. 26-2. A. C. polarogram of cadmium, nickel, cobalt, zinc, iron and manganese
Supporting electrolyte, NH_4ClO_4 0.42 M- NH_4OH 1.25 M (tartaric acid 0.008 M-HCl 0.0008 M)

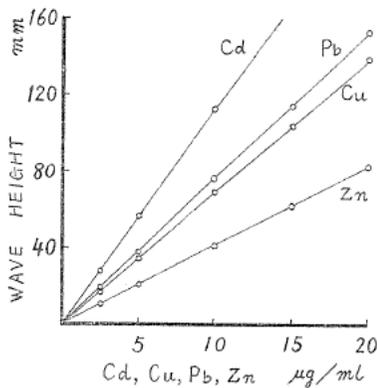


FIG. 27-1. Determination of cadmium, lead, copper and zinc by the polarographic method.

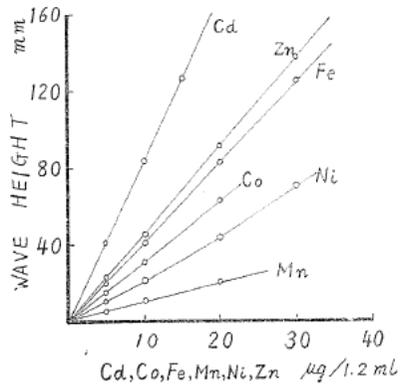


Fig. 27-2. Determination of cadmium, zinc, iron, cobalt, nickel and manganese by the polarographic method.

TABLE 22. Determination of Cu, Pb, Cd, Ni, Co, Zn, Fe and Mn*

Sample	Method	Cu	Pb	Cd	Ni	Co	Zn	Fe	Mn
Sample A	proposed	2.2	1.0	<0.1	43	<0.5	3	44	5.5
	other	2	1		45			45	6
Sample B	proposed	2.0	2.1	<0.1	20	1.6	2	68	4.8
	other	2		<0.1	19	1.5		70	5

*in ppm

shown in Fig. 27 for cadmium, lead, copper, zinc, iron, cobalt, nickel and manganese. The results obtained for typical samples are shown in Table 22.

2.3. Coulometric method

2.3.1. Apparatus

The apparatus constructed for coulometric determination of vanadium is shown in Fig. 28.

For the anodic stripping coulometry of silver, the apparatus shown in Fig. 29 was used.

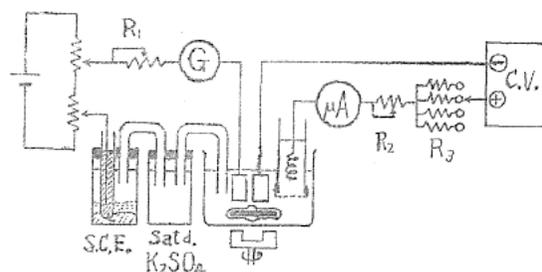


FIG. 28. Apparatus for the coulometric determination of vanadium:
 R_1 1 M Ω , R_2 1 M Ω , R_3 250 K Ω -3 M Ω , G. galvanometer (7×10^{-8} A).

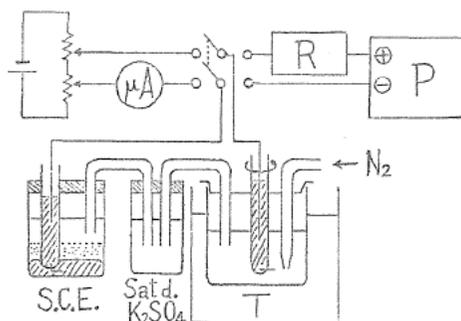


FIG. 29. Apparatus for the anodic stripping coulometry of silver:
 P. polarograph, R. recorder, T. thermostat.

2.3.2. Vanadium

A sample was decomposed with hydrochloric acid and hydrogen peroxide followed by treatment of sulfuric acid. Vanadium was oxidized to vanadate and determined by coulometric titration method.

PROCEDURE

Sample (1 g):

- Decompose the sample with 5 ml of HCl (1+1),
 Oxidize uranium with 1 ml of H₂O₂ (30%),
 Add 2 ml of H₂SO₄ (1+5) to it,
 Evaporate the solution until fumes of sulfuric acid are evolved,
 Cool it and adjust the acidity to about 0.5 N and the total volume of the solution to 20 ml,
 Add 2 drops of potassium permanganate solution (0.3%) to the solution to oxidize vanadium and allow it to stand for few minutes,
 Add 3 drops of sodium nitrite solution (0.7%) to the solution at less than 18°C and stir the solution to decompose the excess of permanganate,
 Add 0.5 g of urea for 25-30 seconds to decompose the excess of nitrite and allow it to stand for 3 minutes,
 Transfer the base solution containing 50 ml of H₂SO₄ (1+5) and 10 ml of ferric sulfate solution (180 g in 5.76 N H₂SO₄), which is equilibrated against 0.72 V (vs. S.C.E.) of platinum electrode potential in an indicator circuit, to the beaker of apparatus,
 Add the sample solution to the beaker,
 Electrolyze it using 100 μ A constant current until the deviation of galvanometer is backed,
 Measure the time required for electrolysis.

↓ Calculate the amount of vanadium using the following equation:

$$V(\text{ppm}) = \frac{\text{electrolysis current (A)} \times \text{time required for electrolysis} \times \frac{1}{66,480} \times 50.95}{\text{Sample taken (g)}} \times 10^6$$

NOTES

- 1) Current used for the electrolysis must be calculated for vanadium content using the equation (suitable time is 100-300 seconds for electrolysis).
- 2) This method serves to determine 1 to 50 ppm of vanadium.

The results obtained by the proposed method are shown in Table 23.

TABLE 23. Determination of Vanadium by the Proposed Method

Sample	Vanadium added (ppm)	Vanadium found (ppm)
A	—	1.1
	7.1	8.0
B	—	0.2
	3.0	2.6

2.3.3. Silver

A sample was decomposed with nitric and sulfuric acids, and silver in this solution was separated by co-precipitation with thallium iodide. After decomposing the precipitate, silver was determined by the anodic stripping coulometry.

PROCEDURE

Sample (1-3 g):

- Decompose the sample with 10 ml of HNO₃ (1+1),

Add 15 ml of H_2SO_4 (1+1) to it,
 Evaporate the solution until fumes of sulfuric acid are evolved,
 Cool and add 100 ml of water to it,
 Add 2 ml of thallosulfate solution (10 mg Tl/ml) and 5 ml
 of potassium iodide solution (5%) to it,
 Allow it to stand,
 Filter the precipitate on a glass filter and with water,

Thallosulfate precipitate containing silver:

Transfer it to 50 ml beaker, and transfer the remaining precipitate on the
 glass filter by dissolving into 1 ml of H_2SO_4 - H_2O_2 mixture (1 N H_2SO_4
 +30% H_2O_2)

Heat the thallosulfate precipitate to dissolve,

Evaporate the solution to dryness,

Cool it and adjust pH to 5-7 using potassium hydroxide and sulfuric acid
 solutions.

Add the solution to calculated volume of potassium sulfate solution to
 adjust the total volume to 10 ml,

Transfer the solution to electrolysis cell,

Rotate the electrode and electrolyze at -0.1 V (vs. SCE) for deposition of
 silver on the platinum electrode (introduce nitrogen to remove the
 dissolved oxygen in the electrolyte for the last 10 minutes of elec-
 trolysis time),

Stop the rotation of electrode and record the stripping current-voltage
 curve by switch on the polarograph and turn the switch Sw on the
 stripping circuit.

Calibration curve is prepared by treating known amounts of silver and blank
 experiment is carried without silver.

NOTES

1) The sample containing more than 0.4 ppm of silver could be determined
 in the presence of large amounts of uranium without preliminary separation. In
 this case, the effect of uranium was suppressed in the form of citrate complex.

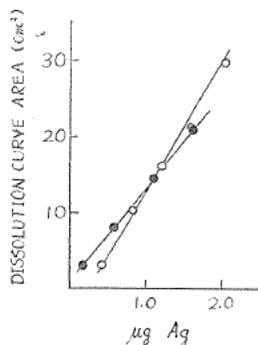


FIG. 30. Determination of silver
 by the anodic stripping method:

- electrolyte 10 ml, 25°C;
- electrolyte 20 ml, 30°C.

TABLE 24. Determination of Silver by
 the Proposed Method

Sample	Silver added (ppm)	Silver found (ppm)
A	—	—
	0.44	0.56
B	—	0.14
	0.30	0.43
	0.44	0.71

- 2) For 10 ml of the electrolyte, electrodeposition for 80 minutes was appropriate, where 0.1-2 μg of silver could be determined.
- 3) pH 3-7 of the electrolyte did not influence the dissolution curve area.
- 4) Less than 1 ppm of silver in uranium metal can be determined by this method.

Calibration curve is shown in Fig. 30.

The results obtained by the proposed method are shown in Table 24.

2.4. X-ray spectrometric method

2.4.1. Apparatus

Norelco X-ray spectrometer was used. A tungsten target tube OEG-50 was used for primary X-rays and lithium fluoride for an analytical crystal. The detector was NaI(Tl)-scintillation counter with pulse height discriminator (type No. 52332 PTA-Unit).

2.4.2. Thorium

Method I (aqueous solution method): A sample was decomposed and uranium was extracted with TBP. Thorium was determined on this solution by fluorescent X-ray spectrometry.

PROCEDURE

Sample (0.3-1 g):

- Decompose the sample with 50 ml of HCl (5 N),
- Oxidize uranium with H_2O_2 (30%),
(Insoluble residue was fused with sodium carbonate, and after dissolving with HCl, the solution was combined in the main solution.)
- Transfer the solution to 100 (or 150) ml separatory funnel,
- Extract uranium by shaking with 50 ml of TBP-benzene solution (3+7) three or five times,

Aqueous phase:

- Wash the aqueous phase with 10 ml of benzene to remove the remaining TBP and discard the organic phase,
 - Evaporate the aqueous phase to few ml on a water bath,
 - Add 1 ml of strontium solution (0.298 mg Sr/ml) to it,
 - Transfer the solution to the sample vessel of X-ray spectrometer,
 - Measure the intensity of SrL_α and ThK_α using fixed count method (the fixed count value used was 12800 counts),
 - Calculate the $I_{\text{Th}}/I_{\text{Sr}}$ ratio and determine thorium content using calibration curve or calculating by experimental equation.
 - Calibration curve is prepared by measuring $I_{\text{Th}}/I_{\text{Sr}}$ using known amounts of thorium and 1 ml of strontium solution as above.
- Experimental equation is as follows:

$$\text{Th}(\text{mg}) = \frac{I_{\text{Th}}}{I_{\text{Sr}}} \times \frac{a}{k}$$

I_{Th} : intensity of ThL_α , I_{Sr} : intensity of SrK_α

a : amount of strontium added as an internal standard (mg)

k : intensity ratio of emitted radiation of the elements by irradiation with a beam of primary X-ray.

Method II (filter paper method): A sample was decomposed and uranium was extracted with TBP. The aqueous phase was absorbed with strontium solution as an internal standard on a filter paper and thorium was determined by fluorescent X-ray spectrometry.

PROCEDURE

Sample (0.5-1 g):

Decompose the sample with HCl and H₂O₂, and extract the uranium with TBP as Method I,

Aqueous phase:

Evaporate the aqueous phase to about 1 ml on a water bath,

Add 1 ml of strontium solution (1.15 mg Sr/ml) to it,

Immerse six sheets of filter paper in the solution,

Dry and transfer them to the sample vessel,

Cover them with Tetron film,

Record the spectra of ThL_{α1}, SrK_α, etc. from 28.5° to 23.5°,

Measure their intensities (I_{Th} and I_{Sr}) from their peak height,

↓ Calculate the intensity ratio I_{Th}/I_{Sr}.

Calibration curve is prepared by treatment of known amounts of thorium as above without extraction.

NOTE

Method I serves to determine more than 50 ppm of thorium and Method II serves to determine more than 20 ppm of thorium.

The sample vessel is shown in Fig. 31 and the calibration curves are shown in Fig. 32.

The results obtained by the proposed method are shown in Table 25.

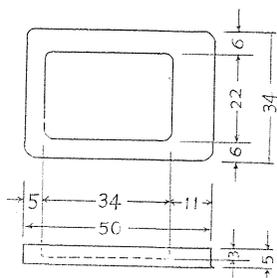


FIG. 31. Acrylic plastic sample vessel (in mm).

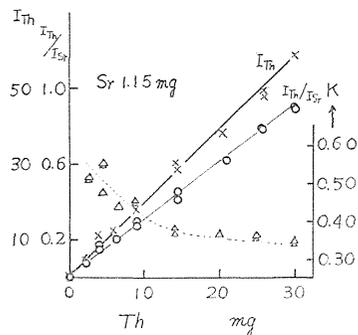


FIG. 32. Determination of thorium by the X-ray spectrometry (filter paper method): 40 kV, 23.5 mA, Sf 8×8.

TABLE 25. Determination of Thorium by the Proposed Method

Thorium found (%)		Photometric
Method I	Method II	
0.049 (10 detns) σ 0.002	0.049 (15 detns) σ 0.002	0.055

2. 5. Spectrographic methods

2. 5. 1. Apparatus

Shimadzu QL-170 spectrograph was used.

2. 5. 2. Nickel, aluminum, chromium, manganese, calcium and copper

Traces of impurities in uranium metal was determined by A. C. arc spectrography after extraction of uranium with TBP.

PROCEDURE

Sample (0.5 g):

Decompose the sample with 10 ml of HNO₃,
 Evaporate the solution to 5 ml,
 Add 10 ml of water to it,
 Transfer the solution to 100 ml separatory funnel,
 Extract uranium by shaking with 15 ml of TBP-CCl₄ (3+7),
 Reject the organic phase and repeat the extraction of uranium,

Aqueous phase:

Transfer the aqueous phase to 50 ml quartz evaporating dish.
 Evaporate the solution to 0.5 ml,
 Add 3 ml of HCl (1+1) to it and evaporate to 0.5 ml,
 Add 3 ml of HCl (1+1) to it and evaporate to 0.5 ml,
 Add 100 mg of graphite powder to the solution and ferric chloride so as
 to amount to 100 ppm of iron,
 Evaporate the mixture to dryness,
 Transfer 10 ml of the sample powder to graphite electrode,
 ↓ Excite the spectra

Calibration curves are prepared by treating known amounts of metals as above.

NOTES

1) Experimental conditions used were as follows:

Excitation	100 V, 8 Ω
Slit width	10 μ
Analytical gap	2 mm
Pre-arc time	none
Exposure time	60 sec
Filter	none
Emulsion	Fuji process
Photo processing	FD-131, 20°C, 4 min. FF-H 4, 20°C, 10 min.
Analytical line pair	Ni I 3050.8 A/Fe I 3047.6 A Al I 3092.7 A/Fe I 3047.6 A Cr II 2835.6 A/Fe II 2755.7 A Mn I 2798.3 A/Fe I 3047.6 A Ca II 3158.8 A/Fe I 3047.6 A Cu I 3247.5 A/Fe I 3047.6 A

2) Dimension of graphite electrode is shown in Fig. 33.

The results obtained by the proposed method are summarized in Table 26.

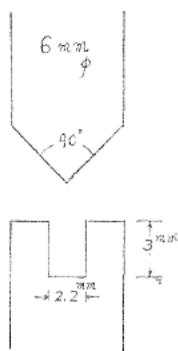


FIG. 33. Graphite electrode.

TABLE 26. Determination of Ni, Al, Cr, Mn, Ca and Cu by the proposed method

No. of exp.	Found (ppm)					
	Ni	Al	Cr	Mn	Ca	Cu
	20.5	9.9	4.1	6.0	5.1	7.1
	20.5	10.4	4.8	6.0	5.5	8.0
	21.2	9.6	4.6	5.0	3.7	7.7
	20.5	10.0	5.0	6.0	4.8	8.1
Chemical	21.0	11	6.2	6.1		5.5

2.5.3. Rare earths

Rare earths in uranium metal was determined by copper spark spectrography. TBP-and cyclohexanone-extraction were used for separation of uranium and thorium.

PROCEDURE

Sample (20 g):

- Decompose the sample with 200 ml of HCl (3+2) and 20 ml of H₂O₂ (30%),
- Evaporate the solution to 100 ml,
- Transfer the solution to 300 ml separatory funnel,
- Extract uranium by shaking with 50 ml of TBP-CCl₄ (1+1),
- Reject the organic phase and repeat the extraction of uranium,

Aqueous phase:

- Transfer the aqueous phase to 100 ml beaker,
- Evaporate the solution to dryness,
- Add 10 ml of HNO₃ (1+1) to dissolve the residue,
- Evaporate the solution to 1 ml,
- Add 10 ml of H₂O and 15 g of ammonium nitrate to it,
- Transfer the solution to 100 ml separatory funnel,
- Extract thorium by shaking with 20 ml of cyclohexanone,
- Reject the organic phase and repeat the extraction of thorium three times,
- Reject the organic phase,

Aqueous phase:

- Extract rare earths by shaking with 20 ml of TBP-CCl₄ (3+7) three times,

Organic phase:

- Back-extract rare earths by shaking with 10 ml of HCl (1+10),

Aqueous phase:

- Transfer the aqueous phase to 20 ml quartz evaporating dish,
- Evaporate the solution to dryness,
- Add 200 μ l of ammonium molybdate solution to the residue,
- Transfer 100 μ l of the solution on to a copper electrode and dry it,
- Excite the spectra by copper spark method.

Calibration curves are prepared by treating known amounts of rare earths.

NOTE

Experimental condition used was as follows:

Excitation	Feussner Spark C 0.003-0.006 μ F Parameter L 800 μ H
Slit width	15 μ
Analytical gap	2 mm
Exposure time	90 sec
Electrode	6 mm ϕ
Emulsion	E. K. SA-1
Photo processing	D-19, 20°C, 4 min. FF-H 4, 20°C, 10 min.
Analytical line pair	Y 3832.9 A/Mo 3798.9 A La 3949.1 A/Mo 3903.0 A Yb 3988.0 A/Mo 3903.0 A Sm 3634.3 A/Mo 3798.9 A Eu 3907.1 A/Mo 3903.0 A Gd 3768.4 A/Mo 3798.9 A Dy 4000.5 A/Mo 3903.0 A

The results obtained by the proposed method are shown in Table 27.

TABLE 27. Determination of Rare Earths by the Proposed Method

	Dy	Eu	Gd	La	Sm	Yb	Y
Added (ppm)	0.04	0.03	0.08	0.04	0.09	0.05	0.02
Found (ppm)	0.03	0.03	0.06	0.05	0.04	0.04	0.03

2. 6. Carbon

2.9.1. Gravimetric method

Carbon in uranium metal was converted to carbon dioxide and was determined by absorbing carbon dioxide in solid sodium hydroxide.

APPARATUS

The apparatus is shown in Fig. 34. The combustion tube used for preheater is filled with 10% platinum asbestos for the first half and with copper oxide in screen form for the last half. The sample combustion silica tube is closed with a ground-glass cap containing a magnetic driving device. The carbon dioxide absorber is a U-tube of about 9 g and its total weight including chemicals, is about 16 g. This tube contains sodium hydroxide for two-thirds of the length of the tube and anhydrous magnesium perchlorate granules in the remaining space. U-tubes are coated with a semi-transparent film of gold in order to eliminate the effects of electric charge and moisture on the surface of the tubes, and to weigh them quickly and accurately.

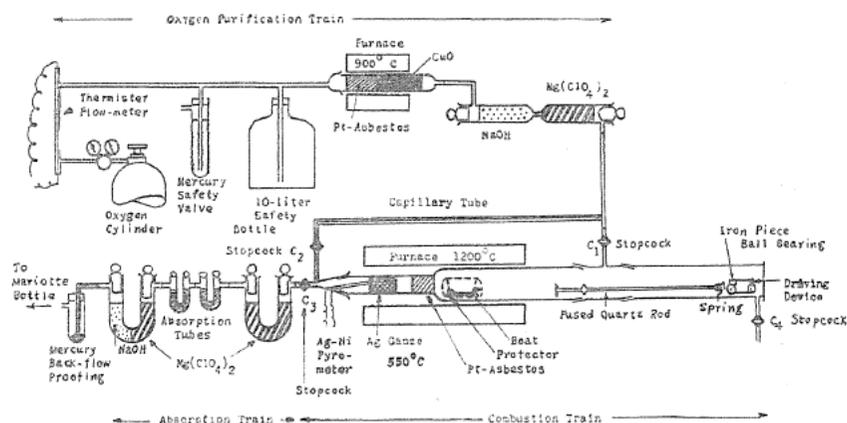


FIG. 34. Apparatus for determination of carbon.

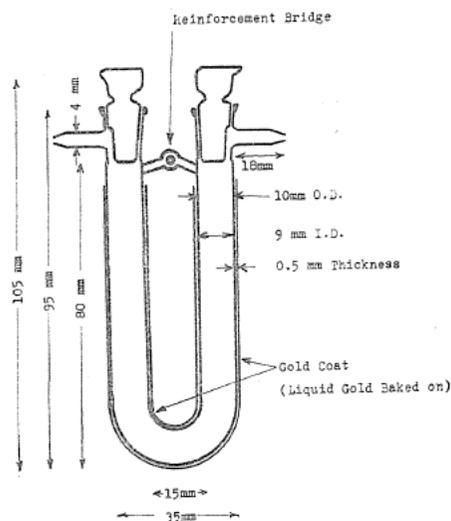


FIG. 35. Gold coated absorption tube.

PROCEDURE

Sample (1 g):

- Place the sample in a silica boat ($5 \times 15 \times 100$ mm),
- Transfer the boat into the entrance of the combustion tube,
- Close the stopcock C_1 , and open the stopcock C_2 and C_4 to sweep out entire air completely from the combustion chamber with purified oxygen flow at a rate of 250 ml per minute for 4 minutes,
- Connect the absorption tubes to the train,
- Close the stopcock C_2 and C_4 ,
- Open the stopcock C_1 and push the boat in to the furnace with magnet driving unit,

- Open the stopcock C_3 to adjust oxygen stream passing through the absorption tubes at a rate of 60 ml per minute until the exhaust of oxygen amounts to 1 liter,
- Disconnect the absorption tubes, and allow the tubes to stand for 15 minutes in the balance case,
- ↓ Weigh the absorbing tubes, and determine the carbon content.

NOTES

- 1) Blank correction was practically unnecessary after running 30 hours' pre-ignition.
- 2) This method is suitable for the determination of 10 μg to 1000 μg of carbon, and is performed within 50 minutes with satisfactory precision.

2.6.2. Titrimetric method

Carbon in uranium metal was converted to carbon dioxide and was absorbed in barium hydroxide solution. Excess barium hydroxide was titrated with hydrochloric acid solution.

APPARATUS

Oxygen purification train and combustion train for gravimetric methods are applicable without any change to titrimetric method. The absorbing U-tube is removed and new carbon dioxide absorber (Fig. 36) is used.

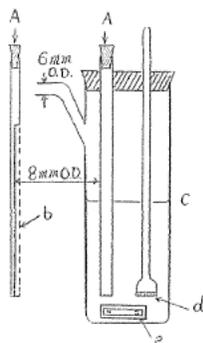


FIG. 36. Carbon dioxide absorber: a. rubber stopper, b. sliced off, c. water level (approx. 5 cm from bottom), d. fritted glass disk, e. rotator (polyethylene coated).

PROCEDURE

Sample (1 g):

- Place the sample in a silica boat,
- Transfer the boat into the entrance of the combustion tube,
- Close the stopcock C_1 and C_3 , and open the stopcock C_2 and C_4 to sweep out entire air completely from the combustion chamber with purified oxygen flow at a rate of 500 ml per minute for 2 minutes,
- Close the stopcock C_4 and open the stopcock C_3 ,
- Pipet 25 ml of absorbing solution (1 liter of 1/300 N barium hydroxide solution, 2 ml of thymol blue-cresol red mixed indicator solution and 1 ml of iso-amyl alcohol) into the absorber introducing air,
- Stop the end of the tube of absorber and close the stopcock C_2 and C_3 ,
- Open the stopcock C_1 and rotate the magnetic stirrer at a rate of 3600-

4000 rpm,
Push the boat into the furnace with magnet driving unit,
Open slowly the stopcock C₃ to adjust oxygen stream passing through the absorber at a rate of 200-250 ml per minute until the exhaust of oxygen amounts to 1 liter,
Close the stopcock C₃ and stop rotation of magnetic stirrer to float up bubbles,
Rotate the stirrer at a rate of 500-1000 rpm and titrate the remaining barium hydroxide with HCl (N/120).

NOTES

- 1) Iso-amyl alcohol allows the bubbles to distribute in the absorbing solution.
- 2) This method is suitable for the determination of 40 to 500 μg of carbon and requires less than 10 minutes per a determination.

2.6.3. High-frequency method

A sample was combusted and the carbon dioxide resulted was absorbed in diluted barium hydroxide solution. Carbon amount was determined by change of the plate current of high-frequency oscillating tube.

APPARATUS

Oxygen purification train and combustion train for gravimetric methods are applicable without any change to high-frequency method. The absorption train was removed and sulfuric acid-chromic acid bead tube and newly designed absorption cell, equipped with a submersion type condenser electrode were substituted for absorption train. Fig. 37 shows the absorption cell. Submersion type condenser electrode is shown in Fig. 38 and oscillator circuit in Fig. 39.

PROCEDURE

Sample (1 g):

(Operations before sweeping out of air from combustion chamber are exactly the same as described in gravimetric method.)
Pull out the thermometer from the absorption cell opening on the rubber stopper,
Add the sample to 20 mg of fine powdered barium carbonate and required volume of absorption solution through that opening, and re-insert the thermometer again to close the opening,
Adjust the variable resistance R in Fig. 39 so as to balance the bridge and microammeter (50 μA full scale) points to zero,
Rotate the magnetic stirrer under the cell at a speed of 1000 rpm,
Close the stopcock C₂ and C₄ and open the stopcock C₁,
Push the boat into the furnace with magnet driving unit,
Open slowly the stopcock C₃ to adjust oxygen stream passing through the absorption cell at a rate of 200-250 ml per minute until the exhaust of oxygen amounts to 1 liter,
Stop rotation of the magnetic stirrer,
Read denotation of the microammeter.

Calibration curve is prepared by treatment of known amounts of sucrose as above.

NOTES

1) Temperature change of the absorption solution before and after the absorbing procedure affects to the denotation of micro-ammeter. A linear relationship between these factors is observed from 15° to 25°.

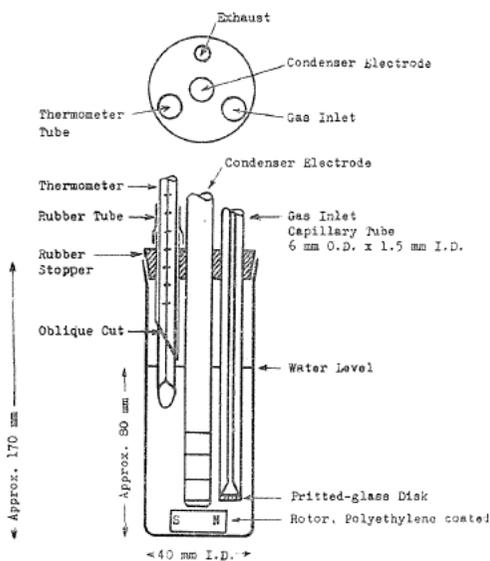


FIG. 37. CO₂ Absorber, Equipped with Condenser Electrode.

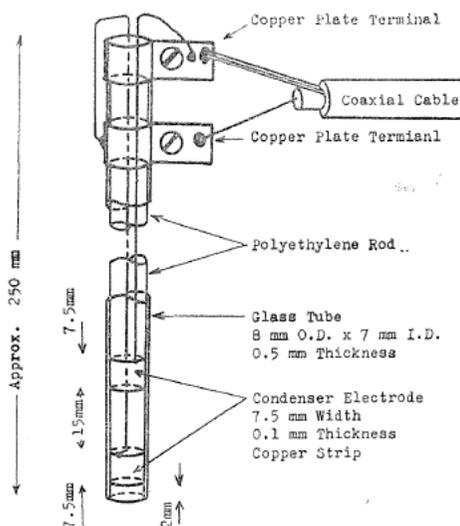
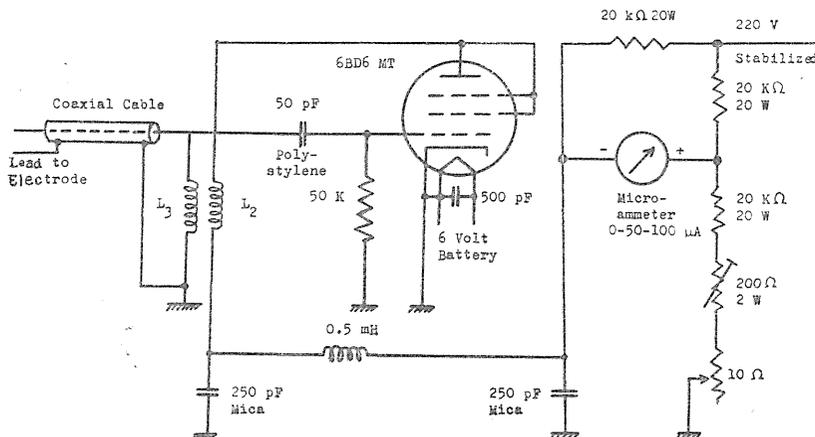


FIG. 38. Submersion Type Condenser Electrode.



Coils: L_2 0.3 mm wire 4 turns on 14 mm bobbin, space winding.

L_3 0.3 mm wire 6 turns on the same bobbin, space winding.

FIG. 39. 30 Mega cycles oscillation circuit.

2) Powdered barium carbonate is added for rapid deposition of barium carbonate precipitate in the absorbing solution.

3) A linear relationship between denotation of the micro-ammeter and carbon amounts is observed from 10° to 30° .

4) This method is suitable in the range of 90 to $500 \mu\text{g}$ of carbon, and carbon determination can be performed within 8 minutes.

Analytical results on uranium metals are given in Table 28.

TABLE 28. Determination of Carbon by the Proposed Methods

Sample	Carbon found (ppm)		
	Gravimetric	Titrimetric	High-frequency
A	313, 302, 315	—	304, 310, 293, 298
B	114, 113, 106	—	—
C	421, 398, 414	—	—
D	349	359, 347, 365, 351	—

3. Discussion

Spectrophotometric method has been popular and indeed, has a sensitivity adequate for determining trace constituents. Therefore, the principal works were made by spectrophotometric method in this study, too. Boron and cadmium are impurities which are difficult to determine because of trace amounts and of contamination in the course of the analysis. Great care must be taken of to prevent contamination in the determination of boron. Curcumin is satisfactory as a spectrophotometric reagent for boron, compared with other reagents. When any contamination is prevented 0.05 ppm of boron can be determined. Cadmium can be determined by dithizone method without error after extraction of cadmium as an iodo-complex. This method of separation is suitable for determining trace

amounts of cadmium.

For the determination of phosphorus, silicon and arsenic, a methyl iso-butyl ketone extraction of molybdo-phosphoric, silicic or arsenic acid is applied. Arsenic is preliminarily separated by extracting with carbon tetrachloride in a solution containing perchloric and hydrochloric acids and potassium iodide. Silicon is present in the form of acid-soluble and acid-insoluble silicon. Therefore, carbonate fusion method is proposed for determining total silicon.

The proposed methods of spectrophotometric determination of impurities in uranium metal give reliable and accurate results.

Table 29 shows the results obtained by the proposed method and a comparison with the results obtained in other laboratories using the proposed method or other methods.

TABLE 29. Analytical Results of Uranium Metal
Impurities obtained (ppm)

Element	method	Nagoya University	Other laboratories					
			A	B	C	D	E	F
B	proposed other	0.12	0.16		0.11			0.15
Cd	proposed other	<0.02		<0.1	<0.1			<0.1
Co	proposed other	1.6	1.6	1.2	1.3	1.4	1	1.1 1.1
Cu	proposed other	1.7	2.6	1.6	1.9	1.5	1.9	1.5 * 1.5
Fe	proposed other	67	71	75	70	72	79	71 69
Mn	proposed other	4.7	5.3	4.5	4.7	4.5	4.4	4.4
Ni	proposed other	19.3	18.9	19.1		18.1 19.7	18.8 19.4	19.2 20.2
N	proposed other	23	25	21	24		22	20 20
P	proposed other	11	11	12	10	12 12	14 12	12
Si	proposed other	63	53	51		58 55	55 48	
Th	proposed other	2.7	9.5	20.7		7.5	5.2	<10

TABLE 30. Determination of Impurities in NBL Analyzed Sample
by the Proposed Method

Element	Impurities found (ppm)		Remarks
	NBL analyzed value	Proposed method	
Fe	45	44.4 44.6	U separated U not separated
Ni	45	44.4	
Mn	6	5.4	
Pb	1.0	1.1	
Si	51	54.7	
Th	0.3	0.4	
C	410	411	Combustion- gravimetric

The results obtained for NBL analyzed sample No. 16 are shown in Table 30.

A. C. polarographic method is a suitable technique for cadmium, which is more accurate than the dithizone spectrophotometry, and this method provides a simultaneous determination of various elements. After separation of uranium by extraction with TBP, copper, lead, cadmium, zinc, nickel, cobalt, iron and manganese are determined using a suitable supporting electrolyte. Chlorine can be determined by A. C. polarography under simple manipulation. This method is superior to other methods of determination in simplicity and sensitivity.

Coulometric method is suitable for the determination of traces of vanadium because of lack of spectrophotometric method for vanadium in uranium metal. Traces of silver is determined conveniently using anodic stripping coulometry.

Spectrographic method is suitable for simultaneous and rapid determination of various trace elements. The proposed TBP-extraction-A. C. arc method is satisfactory for determining nickel, aluminum, chromium, chromium, manganese, calcium, copper etc. in uranium metal. Rare earths are determined only by spectrographic method. The proposed copper spark method is suitable for the determination of rare earths.

Thorium in uranium metal can be determined conveniently by X-ray spectrometry. This technique will be applied to the determination of other impurities in uranium metal.

Carbon is an important element to be determined from the standpoint of its effect on metallurgical property of uranium metal. In this study three methods were examined and developed for the determination of carbon. These are gravimetric, volumetric and high frequency methods. High-frequency method is suitable for the routine determination of carbon.

Acknowledgements

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List of Research Papers

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- 11) Determination of trace amounts of vanadium in metallic uranium by the coulometric titration.
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