Dibenzoylmethane as a Chelating Reagent in Solvent Extraction and Spectrophotometric Determination*

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Solvent extraction of ferric iron, uranium, beryllium, copper, nickel, cobalt and zinc as a chelate with dibenzoylmethane were studied using butyl acetate or chloroform as an extracting solvent. And its applications to the spectrophotometric method for the determination of iron and uranium were also investigated.

Quantitative extraction can be obtained in the following pH range ; pH 2-3 for iron, pH 5-9 for uranium, beryllium and copper, pH 8-10 for nickel, pH 9-10 for zinc and near pH 10 for cobalt. Among these metals, uranium and beryllium are extracted even in the presence of EDTA. With the information on the extraction behaviours of these metal chelates, the methods for the separation of uranium and beryllium from fission products, the separation of iron from copper, nickel and cobalt, and the separation of copper from nickel and cobalt were examined.

Crystals of ferric- and uranyl chelate were prepared and the compositions were estimated to be $Fe(C_{15}H_{11}O_2)_3$ and $UO_2(C_{15}H_{11}O_2)_2$. Ferric- and uranyl chelates in organic solvent exhibit absorption bands in and near ultraviolet region, and the maxima at $410m\mu$ of iron and at $400m\mu$ of uranium can be used for the spectrophotometric determination. Beer's law is obeyed up to 2 ppm of iron and 10 ppm of uranium. Molar extinction coefficient of iron is 17,000 1/M cm at $410m\mu$ and of uranium 20,300 1/M cm at $400m\mu$ and 17,680 1/M cm at $410m\mu$. By the analytical procedure proposed, 0,00003-0.0001% of iron in nickel, cobalt and zinc salt was successfully determined.

INTRODUCTION

Dibenzoylmethane, one of β-diketones, reacts with many metals to form extractable chelate as acetylacetone or TTA[1]. However the reagent has been used only for the solvent extraction and the spectrophotometric determination of uranium[2].

In the present work, the extraction behaviours of the chelates of ferric iron, uranium, beryllium, copper, nickel, cobalt and zinc were studied, and the spectrophotometric methods for the determination of iron and uranium were investigated in detail, by preparing the crystal of ferric- and uranyl dibenzoylmethane chelate, in order to develope the applicability of this reagent.

Although dibenzoylmethane is somewhat troublesome in comparision with acetylacetone because of its less solubility in water, copper, nickel, cobalt and zinc, of which the former two did not show complete extraction and the latter two could not be extracted by acetylacetone method, can be quantitatively extracted under the optimum condition. From the results obtained, the methods for the

separation of these metals were examined, and the analytical procedures for the determination of iron and uranium were proposed.

APPARATUS AND MATERIALS

Spectrophotometric, polarographic and radioactivity measurements were made with a Hitachi's Photoelectric Spectrophotometer, Model EPU-2A, a Yanagimoto's Polarograph, Model PA-105, and Metro's ElT Scaler, using TEN endwindow type G-M Tube 132A, respectively. A Hitachi-Horiba's Glass Electrode pH Meter, Model M-3 was used for pH measurements,

Uranyl nitrate solution, $20.0\mu gU/ml$: $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved with water. After the concentration was determined by a gravimetric method as U_3O_8, the solution was diluted to an appropriate volume.

Ferric perchlorate solution, $10.0\mu gFe/ml$: Accurately weighed electrolytic iron was dissolved with perchloric acid and hydrogen peroxide. After fuming to almost dryness, the residue was dissolved with water and diluted to a desired volume.

Nickel sulphate solution, $100\mu gNi/ml$ and $1.0\mu g/ml$: Electrolytic nickel was dissolved with nitric acid and fumed with sulphuric acid. The residue was dissolved and diluted with water.

Beryllium sulphate solution, $10.0\mu gBe/ml$: $BeSO_4 \cdot 4H_2O$ was dissolved with 50 ml. of water containing 1 ml of concentrated sulphuric acid, and the concentration was estimated gravimetrically as 2-methyloxinate. The solution was diluted appropriately before use.

Copper sulphate solution, $100\mu gCu/ml$: 982.5 mg of $CuSO_4 \cdot 5H_2O$ was dissolved with water containing a few drops of sulphuric acid and diluted to 250 ml. The solution was diluted tenfold.

Cobalt sulphate solution, ca. $10\mu gCo/ml$: 120 mg of $CoSO_4 \cdot 7H_2O$ was treated in the same manner as copper sulphate.

Zinc sulphate solution, ca. $10\mu gZn/ml$: 110 mg of $ZnSO_4 \cdot 7H_2O$ was treated in the same way as in the case of copper sulphate or cobalt sulphate.

Cobalt-60, zinc-65 and fission products*: These solutions were obtained from ORNL. They were diluted to give $0.1\sim0.5\mu C/ml$ on cobalt-60 and zinc-65, and $1\sim5\mu C/ml$ on fission products.

Dibenzoylmethane solution, 5%: 5 g dibenzoylmethane was dissolved and diluted to 100 ml with acetone.

EDTA solution, 10%.

Eriochrome Cyanine R solution, 0.1%: 250 mg of the reagent was dissolved with water, and diluted to 250 ml after 1.25 g of sodium chloride, 1.25 g of ammonium nitrate, 0.5 ml of concentrated nitric acid and 25 ml of ethyl alcohol were added.

Dimethylglyoxine solution, 1% alcoholic solution.

Chloroform and butyl acetate: Chloroform was purified by washing with diluted sodium hydroxide solution, water, diluted hydrochloric acid and three portions of water, followed by distillation. Butyl acetate was purified by washing with water and by distillation.

All other reagents used in this experiment were the reagent grade materials.

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* Batch No. 39

EXPERIMENTAL AND RESULTS

1. Procedure for the Extraction of Metal Dibenzoylmethane Chelates

To about 30 ml of a sample solution, whose pH is adjusted to a desired value, 5% dibenzoylmethane-acetone solution is added, and the solution is warmed on a water bath at about 70°C to melt the reagent for 10~20 minutes. After cooling, the solution with suspended excess reagent is transfered to a 100 ml separating funnel, diluted to 50 ml and shaken with 20 ml or 10+5+5 ml of chloroform or butyl acetate, for 10~15 minutes.

Five millilitres of 0.5M acetic acid or 0.5M boric acid were used as a buffer solution, when pH value changed remarkably by the extraction. EDTA was also employed as a masking agent in the extraction of uranium and beryllium. In this case, 2 ml of 10% EDTA solution and calcium chloride solution equivalent to EDTA were added to the sample solution. As an extracting solvent, butyl acetate seemed to be better, except for the extraction of beryllium, where chloroform was convenient.

2. Procedure for the Determination of Extractability

Iron and Uranium: Extractability of iron and uranium were obtained by measuring absorbance of organic layer*. The organic solution containing a known amount of ferric dibenzoylmethane or uranyl dibenzoylmethane chelate was used as a standard of the spectrophotometric determination.

Beryllium: Extraction recovery was estimated colorimetrically by Eriochrom Cyanine R method. Extracting solvent combined in a beaker is evaporated and organic matter is decomposed by fuming with perchloric acid. The residue is dissolved with 20~30 ml of water, then 5ml of 5% sodium acetate solution, 1 ml of 10% EDTA solution and 5 ml of Eriochrome Cyanine R solution are added, and pH is adjusted to 9.7-9.8. After the resulting solution is diluted to the mark in a 50 ml volumetric flask, absorbance is measured at 510mμ against the reagent blank.

Copper: Extractability was measured polarographically. Copper in organic solvent is backextracted with 10+5+5 ml of 6N hydrochloric acid, which are combined and evaporated to nearly dryness. Residue is dissolved with water, and diluted to 20 ml after 5 ml of 4M ammonium chloride-4M ammonia mixture is added. An aliquot of this solution is taken, air is removed with nitrogen, and the polarogram is recorded.

Nickel: Extraction recovery was determined colorimetrically by dimethylglyoxime method. Nickel is backextracted with 10+5+5 ml of 0.5N hydrochloric acid solution which is evaporated to almost dryness. Residue is dissolved with water and transfered to a 20 ml volumetric flask. Five milliliters of 5% tartaric acid, 0.2 ml of bromine water are added and ammonia water is then added until colour of bromine disappears and more 1ml excess. After 2 ml of 1% dimetylglyoxime solution is added, the resulting solution is diluted to the mark, and absorbance is obtained at 450mμ.

Cobalt and Zinc: Extractability of cobalt and zinc were given by radioactivity measurements, using cobalt-60 and zinc-65 as a tracer. Each 2 ml of organic

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* See the analytical procedure described in following section.

and aqueous layers is pippetted into a stainless steel dish, 25 mm in diameter and 5 mm in hight, and evaporated under a infrared lamp. Distribution ratio (D) is obtained by measuring radioactivity and per cent extraction (E) is calculated by the following equation,

$$E(\%) = \frac{100\,D}{D+2.5}$$

If organic layer creeps over the dish, the solvent layer is stripped with 0.5N hydrochloric acid and acid layer is used for counting. When aqueous layer contains relatively a large amount of salt, extraction recovery is estimated by comparing radioactivity of organic layer with the standard which is prepared by diluting to the same concantration as that of the sample solution, but without addition of buffer solution etc..

3. Extraction of Metals

Effect of reagent concentration. Effect of the added amount of dibenzoyl-methane was studied, and the results on iron, uranium, beryllium and copper were shown in Fig. 1, which were obtained at optimum pH of each metal, namely pH 2.0–3.0 for iron, pH 6.0–7.0 for uranium and beryllium, and pH 5.0–6.0 for copper. Iron, uranium and copper were extracted with butyl acetate, but beryllium with chloroform. Figure 1 indicates that iron and uranium are quantitatively extracted by adding 0.2 ml of 5% reagent solution, beryllium 0.4 ml, and copper 0.7 ml, respectively. Nickel, cobalt and zinc behave in the similar manner as copper.
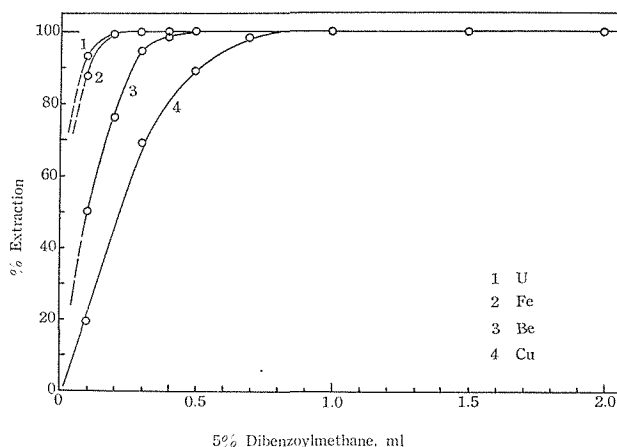

Fig. 1. Effect of reagent concentration.

From these results, it was decided that 0.5 ml of 5% dibenzoylmethane acetone solution was used for the extraction of iron, uranium and beryllium, while 1 ml for the other metals.

Effect of pH. Effect of pH on the extractability was investigated and the extraction curves were shown in Fig. 2.

The pH region where the quantitative extraction can be attained are 2–3 for iron, 5–9 for uranium, beryllium and copper, 8–10 for nickel and 9–10 for zinc. Cobalt is also extracted near pH 10. In the presence of EDTA only uranium and

beryllium are extracted, and the pH range corresponding to complete extraction is from 6 to 8. Ammonium chloride-ammonia buffer solution gives considerable influence to the extraction of copper, nickel, cobalt, and zinc, especially in higher pH region. It may be due to the formation of ammine complex which is not easily converted to dibenzoylmethane complex.
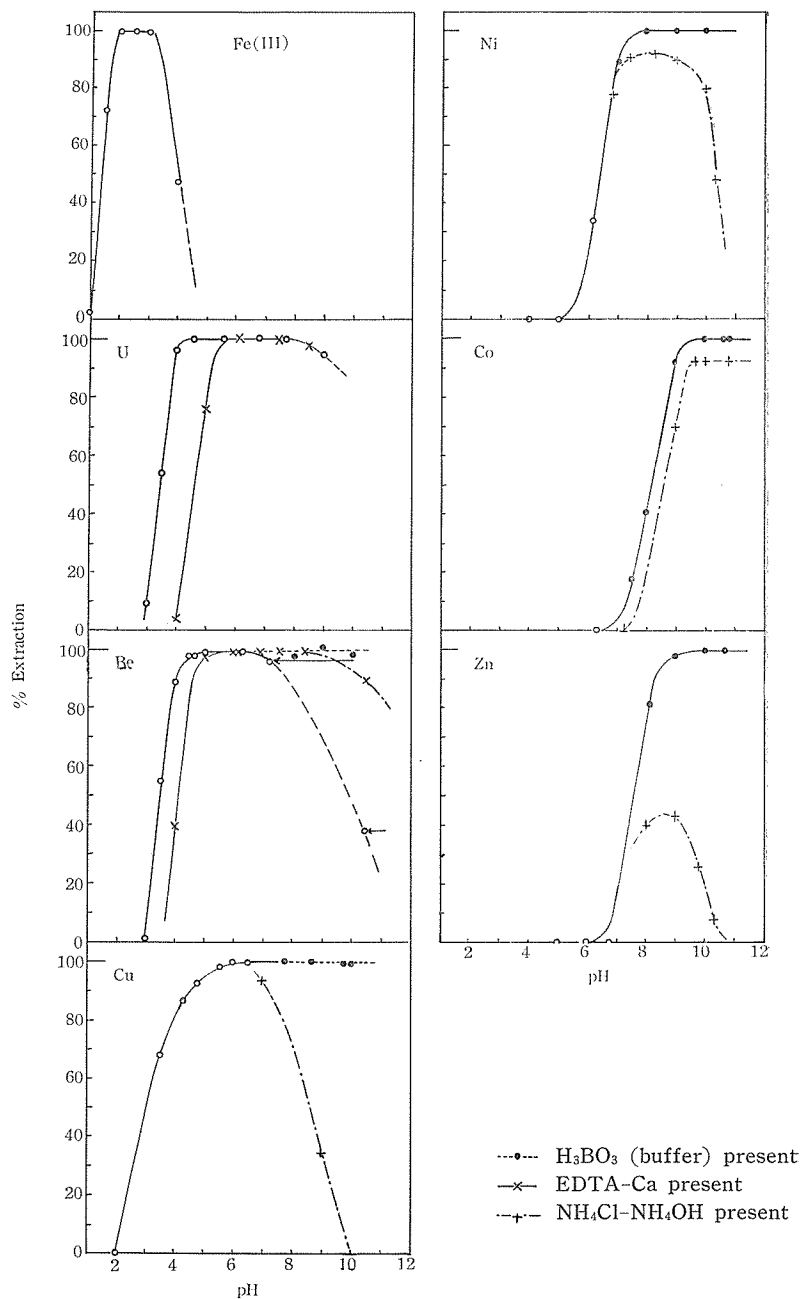

Fig. 2. Extraction curves of metal chelates.

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4. Methods for the Separation of Metals

With the information on the extraction behaviours of metals mentioned above, the application of the extraction procedure to the separation of metals was examined.

Separation of uranium or beryllium from fission products. Extraction was made on a sample solution containing $100\mu g$ of uranium or $10\sim20\mu g$ of beryllium and fission products (gross β : $2\sim3\times10^5$ cpm.), in the presence of EDTA and equivalent calcium chloride. Extracting solvent used was butyl acetate for uranium and chloroform for beryllium, and pH range was from 6.6 to 7.0.

Uranium and beryllium could be completely extracted into organic layer, whereas radioactivity of solvent layer was only a few counts per minuites. The extraction procedure, therefore, can be successfully applied to the separation of uranium and beryllium from mixed fission products with decontamination factor of $10^4\sim10^5$.

Separation of iron, copper, nickel and cobalt. Two steps extraction was made at pH 2 and then at pH 5, on a sample solution containing iron, copper, nickel and cobalt. By the first extraction at pH 2, iron is extracted into butyl acetate layer, and copper is extracted by the second extraction at pH 5. Extraction recovery of iron was 98% or more, and contamination of the other metals were negligible, when organic layer was washed with an appropriate volume of water of pH 2. By the successive extraction at pH 5, extraction yield of copper was $95\sim96\%$. Contamination of iron was less than 1%, and the extractability of nickel and cobalt were 0.5% or less and $1\sim2\%$, respectively. Therfore the extraction using dibenzoylmethane may be used for the separation of iron from copper, nickel and cobalt, and of copper from nickel and cobalt.

5. Method for the Spectrophotometric Determination of Iron and Uranium

Iron- and uranium dibenzoylmethane chelate extracted with organic solvent exhibit absorption bands near ultraviolet region, and it seemed that the extraction procedure can be developed to the spectrophotometric determination of these metals.

Preparation of ferric- and uranyl dibenzoylmethane chelate. Ferric chelate : Dibenzoylmethane acetone solution was added to ferric chloride solution and the mixture was neutralised with diluted sodium hydroxide solution. Dark red precipitate formed was filtered, washed with water and hot alcohol, and then dissolved with benzene. After insoluble residue was filtered off, the crystalline chelate was obtained by evaporating benzene. Crude crystal was then purified by recrystallizing twice from acetone. The iron content in air dried ferric dibenzoylmethane chelate was 7.63%; theoretical value is 7.70% calculated from the formula $Fe(C_{15}H_{11}O_2)_3$.

Uranyl chelate : Procedure for the preparation of uranyl chelate was almost the same as ferric chelate, except that neutralization was made with ammonia and acetone is used for dissolving and recrystallization of crystal, because uranyl chelate is not so much soluble in benzene. The uranium content in air dried crystal was 33.40%. Theoretical values are 33.24% for $UO_2(C_{15}H_{11}O_2)_2$ and 25.32%

for $UO_2(C_{15}H_{11}O_2)_2 \cdot C_{15}H_{12}O_2$, and therefore the uranyl chelate is not an addition compound*.
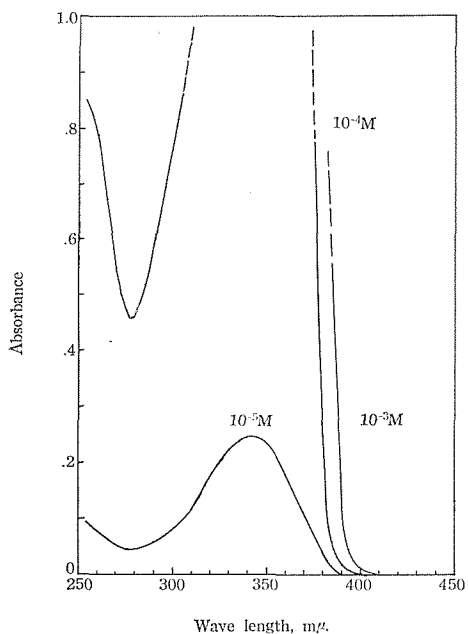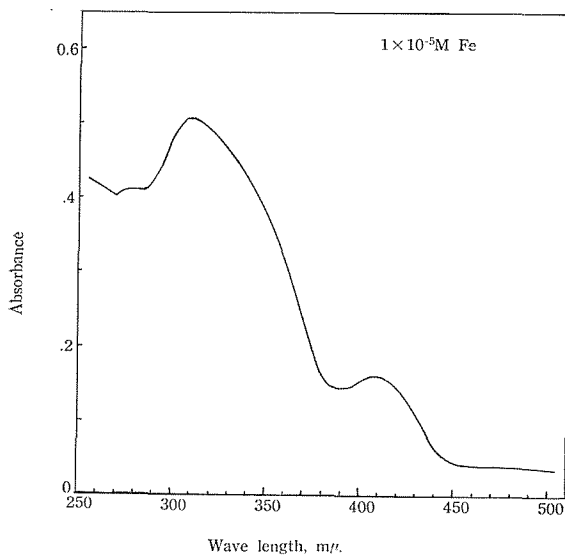

Fig. 3. Absorption spectra of dibenzoylmethane.

Fig. 4. Absorption spectrum of ferric dibenzoylmethane chelate.

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* Uranyl acetylacetonate was a addition compound having formula $UO_2(C_5H_7O_2)_2 \cdot C_5H_8O_2$ [M. Ishibashi, T. Shigematsu, M. Tabushi, J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi), 80, 1018 (1959)].

Absorption spectra of dibenzoylmethane, ferric chelate and uranyl chelate were shown in Fig. 3, Fig. 4, and Fig. 5. As indicated in these figures, ferric chelate shows two absorption bands, of which maxima are at 320mμ and 410mμ, and uranyl chelate gives three maxima at 270mμ, 340mμ and 400mμ. Dibenzoylmethane exhibits, however, extensive absorption in ultraviolet region, and therefore only the absorption maxima at 410mμ of iron and 400mμ of uranium can be used for the determination of these metals.
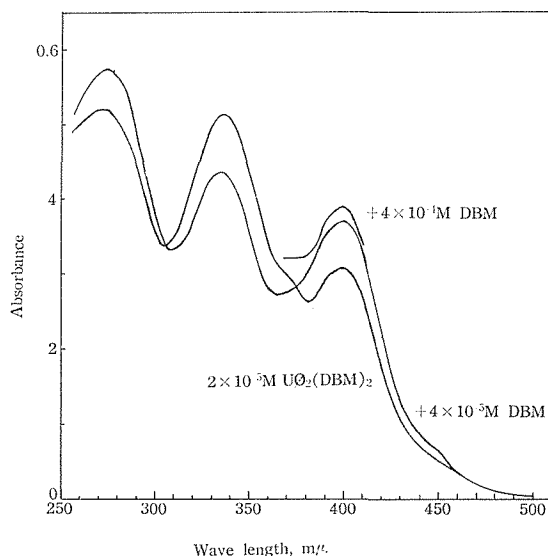

Fig. 5. Absorption spectra of uranyl dibenzoylmethane chelate in butyl acetate.

Determination of iron. Procedure: To a sample solution containing 1~20μg of iron whose pH is adjusted to 2.5-3.0, 0.5 ml of 5% dibenzoylmethane acetone solution is added and the solution is warmed at about 70°C for 10~20 minutes. The complex is extracted with 20.0 ml of butyl acetate, and absorbance of organic layer is measured at 410mμ against the reagent blank.

Table 1. Effect of diverse ion on the determination of iron.

Diverse ion	Added as	Added amount (mg)	Fe found* (μg)	Permissible amount (mg)
Cr^{3+}	Chloride	1	25.2	0.1
Co^{++}	Sulphate	//	20.0	>1
Cu^{++}	//	//	37.3	0.02
Mn^{++}	//	//	20.2	>1
Mo^{6+}	Sodium molybdate	//	∞	0
Ni^{++}	Sulphate	//	19.9	>1
Ti^{4+}	//	//	∞	0
Zn^{++}	//	//	20.1	>1
10% EDTA		2ml	0	0

* Fe present 20.0μg.

Absorption spectrum and calibration curve obtained by the procedure were shown in Fig. 6 and Fig. 7. Beer's law is obeyed and molar extinction coefficient is 17,000 1/M cm at 410mμ.

Table 1 represents the influence of diverse cations. Molybdenum, titanium and large amounts of copper and chromium interfer the determination, but nickel, cobalt, manganese etc. do not give any effect.
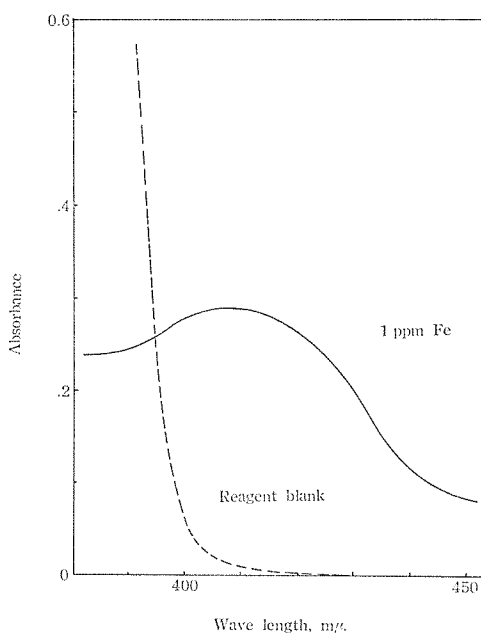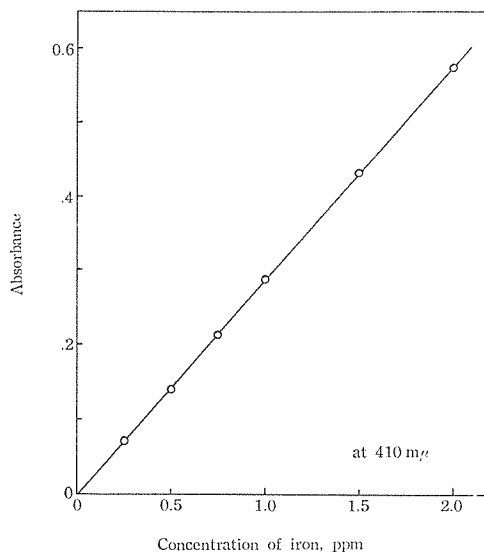
Fig. 6. Absorption spectrum of iron chelate extracted.

Fig. 7. Calibration curve of iron.

Determination of uranium. Procedure : A sample solution containing 5~200μg of uranium is treated in the similar manner as in the case of iron. But 2ml of 10% EDTA solution and calcium chloride equivalent to EDTA are added as a masking agent, extraction is made at pH 6-7 and absorbance is measured at 400mμ or 410mμ.

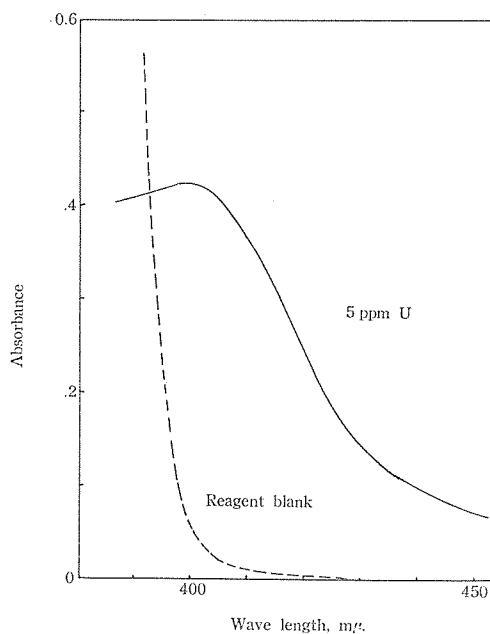Absorption spectrum and analytical curves were indicated in Fig. 8 and Fig. 9.

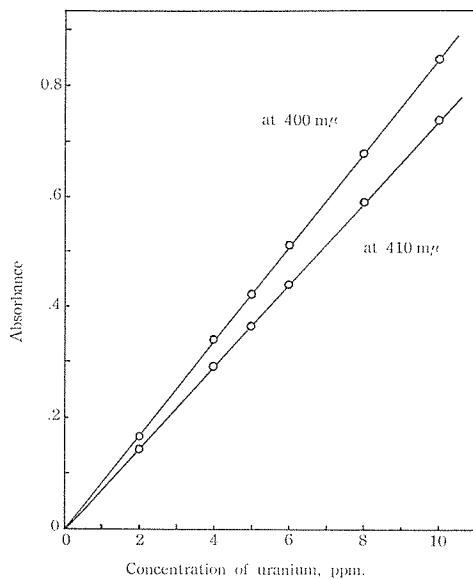Fig. 8. Absorption spectrum of uranium chelate extracted.

Fig. 9. Calibration curves of uranium.

Beer's law is followed up to 10 ppm of uranium, and molar extinction coefficients are 20,300 1/M cm at 400mμ and 17,680 1/M cm at 410mμ.

As represented in Table 2, copper and manganese give a positive error and 1 mg or more of ferric iron, titanium and chromium interfere owing to the precipitation. Influence of thorium, whose extractability is only less than 0.3%, can be minimised by measuring absorbance at 410mμ.

Table 2. Effect of diverse ion on the determination of uranium.

Diverse ion	Added as	Added Amt. (mg)	Detn. at 400mμ		Detn. at 410mμ	
			U found* (μg)	Permiss. Amt. (mg)	U found* (μg)	Permiss. Amt. (mg)
Bi^{3+}	Nitrate	10	100.$_0$	>10	100.$_0$	>10
Cr^{3+}	Chloride	1	ppt	0	ppt	0
Co^{++}	Sulphate	10	103.$_4$	5	103.$_8$	5
Cu^{++}	//	2	114.$_0$	0.1	110.$_0$	0.1
Mn^{++}	//	//	122.$_3$	0.1	116.$_3$	0.1
Mo^{6+}	Sodium molybdate	5	101.$_9$	10	100.$_8$	10
Ni^{++}	Sulphate	10	103.$_4$	5	103.$_0$	5
Th^{4+}	Nitrate	1	103.$_4$	0.5	100.$_9$	1
Ti^{4+}	Sulphate	//	ppt	0	ppt	0
Fe^{3+}	Perchlorate	//	ppt	0	ppt	0

* U present 100μg

Table 3. Determination of micro amount of iron in some samples.

Sample	Amount taken (g)	Fe added (μg)	Fe found (μg)	Fe content (%)
Ni metal*	2.0214		8.47	0.00042
	2.3140		10.07	0.00044
ZnO	5.0		5.2	0.00010$_4$
	10.0		10.8	0.00010$_8$
$ZnSO_4 \cdot 7H_2O$	13.2**		3.8	0.000029
	22.0***		5.7	0.000026
	//		5.5	0.000025
	//	20.0	25.6	0.000025
$NiSO_4 \cdot 7H_2O$	1.0		1.3	0.00013
	2.0		1.9	0.00009$_5$
	//		22.3	0.00011$_5$
$CoSO_4 \cdot 7H_2O$	1.0		1.0	0.00010
	2.0		1.7	0.00008$_5$
	//	20.0	21.7	0.00008$_5$

* After iron contained in the sample was extracted and determined, the extraction recovery was estimated by adding 20.0μg ferric iron to the aqueous phase followed by the similar extraction. Recovery was 101.5$\pm$1.5%.

** 3g as zinc.

*** 5g as zinc.

Determination of iron in nickel, cobalt and zinc. As mentioned above, nickel, cobalt and zinc are not extracted in pH region where ferric iron can be completely extracted, and the decontamination factors of these metals are 5×10^4, $2 \sim 3 \times 10^4$ and 1×10^3 at pH 2.5–3.0. Spectrophotometric method using dibenzoylmethane is therefore employed to the determination of micro amount of iron in these metals or in their salts.

Table 3 showed the analytical results obtained on some samples, such as pure nickel, the reagent grade substances etc.. The results indicate that $0.00003 \sim 0.0001\%$ of iron in these semples of $2 \sim 20$ g in amount, can be analysed by the dibenzoylmethane method.

REFERENCES

（ 1 ） G. H. Morrison, H. Freiser, "Solvent Extraction in Analytical Chemistry" p. 159, John Wiley & Sons. Inc. New York, (1957).

（ 2 ） J. H. Yoe, F. Will, R. A. Black, *Anal. Chem.*, **25**, 1200 (1953) ; P. Blanquet, *Anal. Chim. Acta*, **16**, 44 (1957) ; R. Pribil, M. Jelink, Chem-listy, **47**, 1326 (1953).