

고분자량 아민에 의한 이리듐 제 1 염화주석 착물의 추출 및 분광광도법에 의한 이리듐의 정량법

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Spectrophotometric Determination of Iridium After Extraction of the Stannous-Chloro Complex by High Molecular Weight Amine

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요 약. 염산수용액중에 존재하는 이리듐을 그 분자량 아민(Alamine 336)의 벤젠용액으로 추출한 바 20~100 μg 의 이리듐을 정량적으로 추출할 수 있음을 알았고 이때 이리듐 추출의 가능성에 관하여는 방사성 추적자(Ir-192)를 써서 확인하였다. 유기층에 추출된 화학종의 흡광도를 파장 322.5 nm에서 측정된 결과 본 방법은 이리듐의 정량을 위한 미량분석법으로 사용할 수 있음을 알았다. 이리듐이 아민층에 추출되는 메카니즘에 대한 설명을 시도하였다.

ABSTRACT. About 20~100 μg iridium have been extracted quantitatively as stannous-chloro complex from aqueous solution by Alamine-336, a high molecular weight tertiary amine, dissolved in benzene. The extractability was confirmed by radioactive tracer of iridium-192. The spectrophotometric measurements of the extracted species at 322.5 nm indicate the feasibility of this method to be used as an analytical procedure for the determination of micro amount of iridium. An anion model of stannous-chloro complex of iridium has been postulated to account for the extraction mechanism.

INTRODUCTION

High molecular weight amines(HMWA) have recently attracted the interest of analytical chemists, since such extractions offer wide possibilities for the extraction and purification of metal salts. An extensive investigation on the formation and extraction of group VIII metals was carried out

by Good *et al.*^{1,2}

Recently, Khattak and Magee also applied HMWA in the study for the extraction of chlorotin complex of platinum group elements, e. g., platinum³, palladium⁴ and rhodium⁵.

In the present work a survey of the literature revealed that extraction of iridium into HMWA as the stannous-chloro complexes had not previ-

ously been reported. Therefore, the present investigations were begun in this laboratory with the aim of using HMWA to extract the iridium species and, if possible, use it for the spectrophotometric determination of iridium.

Alamine 336, tricaprylamine, was used as HMWA. The extractability of iridium was evaluated spectrophotometrically and also radiochemically using Ir-192 as a radioactive tracer. The results obtained are reported below.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were carried out with both Beckman DU-2 and DK-2 spectrophotometers using 10.0 mm silica cells.

Samples for extraction were prepared in about 45 ml cylindrical tubes fitted with plastic screw cap stoppers. The samples were then shaken in a box type shaker of A. H. Thomas Co., U. S. A., in which 20 cylindrical tubes were accommodated. Throughout extraction study, the shaker together with the samples were placed in a constant temperature air bath which was maintained at $25 \pm 0.8^\circ\text{C}$.

The counting of radioactivity of Ir-192 was carried out with $2'' \times 2''$ NaI(Tl) well-type Scintillation Detector, Model 422, connected to a Counting Scaler, Model 8775, Nuclear-Chicago, U. S. A.

Lindberg Hevi-Duty furnace was used for chlorination of iridium with the Vycor combustion tubes, 33 mm \times 0.90 m.

Reagents

Iridium Chloride Solution. About 0.3 g of high purity iridium sponge (Johnson and Matthey Chemicals Ltd.) was directly chlorinated⁵ in the presence of sodium chloride for about 8 hours at 700°C . The chlorinated products of iridium were dissolved in 0.1 F hydrochloric acid solution. Because of the possible loss of iridium during

chlorination,⁷ the concentration of iridium solution was determined gravimetrically by hydrolytic precipitation,⁸ which was found to be $293 \pm 3 \mu\text{g/ml}$.

Radioactive Tracer Ir-192 Solution. About 20 mg of iridium sponge were irradiated in the pneumatic tube of TRICA MARK II reactor, Korea Atomic Energy Research Institute, Seoul, for 2 days. The radioactive tracer solution was prepared by dissolving the irradiated iridium (after chlorination) as described above. The iridium concentration of the Ir-192 tracer solution was also determined similarly by hydrolytic precipitation.⁸

Tin(II) Chloride Solution. 23 g of tin(II) chloride dihydrate was dissolved in 100 ml of 3.5 F hydrochloric acid.

Alamine 336. This reagent, also called tricaprylamine (General Mills, U. S. A.) was scrubbed with dilute hydrochloric acid and sodium carbonate solutions to remove lower molecular weight amines and other aqueous soluble impurities.⁸ The reagent was further purified by distilling under the reduced pressure (at ca. 15 mm Hg pressure), and the distillate fraction collected between 234 and 250°C was used. A 0.018 F solution in distilled benzene was used as extractant. All other chemicals were of Analytical Grade reagent.

General Procedure for the Formation and Extraction of Iridium Species. Transfer a suitable aliquot of iridium(IV) solution (20~100 $\mu\text{g Ir}$), contained in 1.00 ml, to an extraction tube. Add 0.53 ml of concentrated hydrochloric acid (12 F) and 1.00 ml of tin(II), and cover the tube with a plastic stopper. Place the tube in a boiling water bath for 2 hours and dilute with water to 10 ml. Add 10 ml of 0.018 F Alamine 336 and shake the system on a mechanical shaker for 1 hour. Allow the phases to separate and filter the amine phase through a

small paper into a silica cell and measure the absorbance at 322.5 nm against the amine blank which is extracted similarly as above. Determine the iridium amount extracted in organic phase by comparing with a calibration curve.

The identical procedure was applied for the extraction of iridium tracer solution, in this case, however, gamma counting was employed to evaluate the iridium activities in both phases after extraction.

RESULTS

Effect of Hydrochloric Acid Concentration.

In order to find the effective concentration of hydrochloric acid for the extraction of iridium (IV), 1 ml of iridium(IV) solution (containing 0.2 mg of Ir) and 1 ml of acid with differing concentrations were warmed on a boiling water bath for two hours. With concentrated hydrochloric acid, the solution remained clear. On decreasing the acid concentrations, however, turbidity was formed. Throughout the test, hydrochloric acid was preequilibrated with Alamine 336.

In order to find the suitable amount of tin(II) chloride for the formation of iridium-tin complex, various amounts of tin(II) chloride, i.e., 1 ml each of 0.01 F and 1 F was added to the iridium solution, obtained as above, which was then warmed on a boiling water bath for two hours. All solutions except the 1 F solution produced the turbidity upon warming. For all subsequent extractions 1 ml of 1 F tin(II) chloride solution was used.

The effect of hydrochloric acid concentration on the extractability of iridium was studied. To the yellow colored solution of iridium-stannous chlorocomplex, obtained by the above procedure, various amounts of hydrochloric acid were added and the aqueous phase was diluted to 10 ml with water which was then extracted with 10 ml of

0.018 F Alamine 336 in benzene on a mechanical shaker for 1 hour. The extraction coefficients were evaluated as follows.

$$\text{Extraction coefficient (E)} = \frac{\text{concentration of metal in organic phase}}{\text{concentration of metal in aqueous phase}}$$

as shown in Fig. 1 and 2, the highest extraction was obtained from aqueous solution 1 F in hydrochloric acid. The radioactivity of Ir-192 tracer in both phases was counted to obtain the data for Fig. 1 and the absorbances of the amine/benzene extract were measured at 322.5 nm for Fig. 2.

Formation of Iridium Complex for Extraction. In the present work, the procedure of Khattak and Magee³⁻⁵ was followed for the formation of extractable species of iridium.

Ten milliliters aqueous solutions, containing both non-radioactive and radioactive iridium(IV) in a solution 1.0 F in hydrochloric acid and 0.1 F in tin(II) chloride, which was prepared by following the procedure given under Experimental, were warmed on a boiling water bath for various length of time. After warming, the iridium solution was shaken with Alamine 336 in benzene for 1 hour. The extraction coefficients were determined by measuring the activities of Ir-192 in both phases, the results are shown in Fig. 3. The absorbances of the amine/benzene extract were measured at 322.5 and 360 nm, respectively, and plotted against the warming times as shown in Fig. 4. These two Figures indicate that the formation of iridium complex is strongly affected by the warming time. It was also concluded that a warming time of approximately 2 hours was adequate for the attainment of equilibrium in the formation of iridium complex, and was used throughout the study.

The shaking time was also examined in similar manner. The aqueous solutions containing iridium

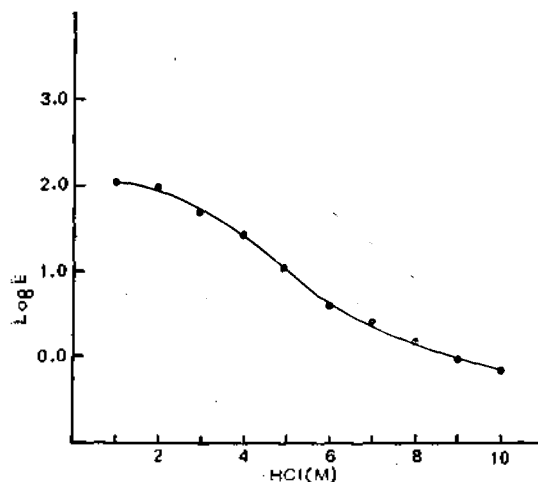


Fig. 1. Extraction of iridium(III)-tin(II) chloro complex by Alamine 336 in benzene at various hydrochloric acid concentrations. E denotes the extraction coefficient.

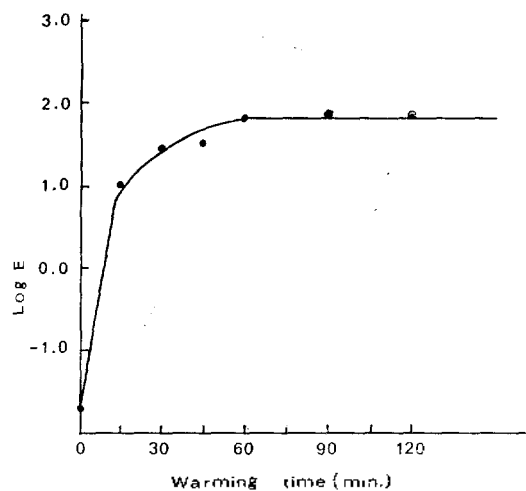


Fig. 3. Effect of various warming times on extraction of iridium(III)-tin(II) chloro complex by Alamine 336 in benzene from 1 M HCl aqueous solution. Warming was done on a boiling water bath. The extraction coefficient (E) was determined with Ir-192 radioactive tracer.

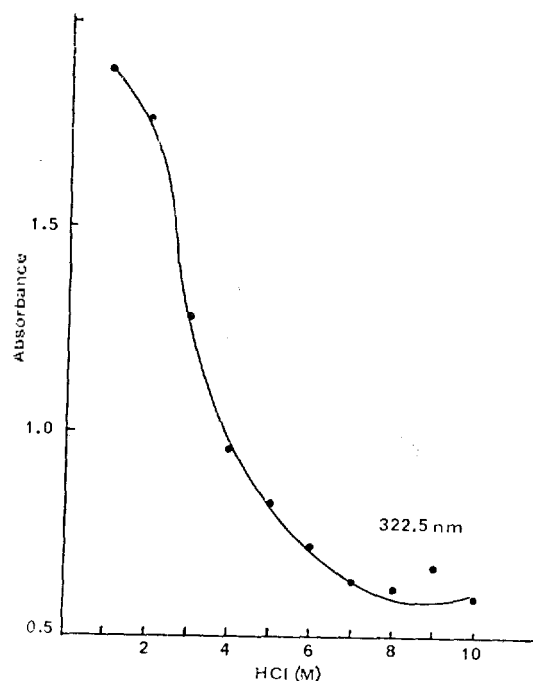


Fig. 2. The absorbance at 322.5 nm of iridium(III)-tin(II) chloro complex extracted by Alamine 336 in benzene at various hydrochloric acid concentrations.

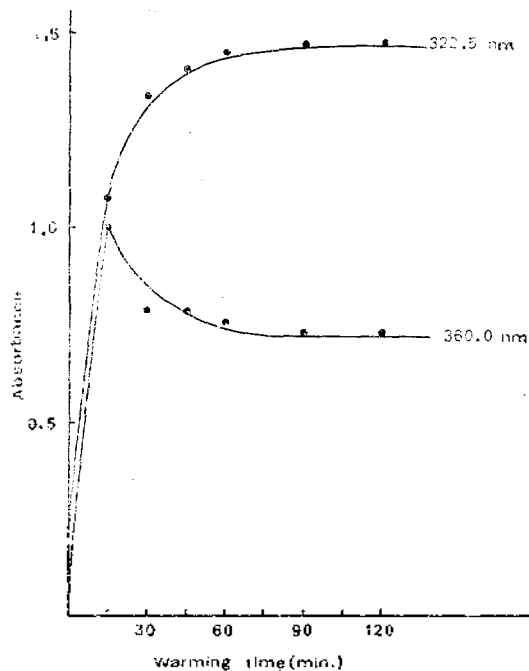


Fig. 4. Effect of various warming times on extraction of iridium(III)-tin(II) chloro complex extracted by Alamine 336 in benzene from 1 M HCl aqueous solution. The absorbances of extracted complex in organic phase were measured at both 322.5 and 360 nm.

complex, formed after warming for 2 hours, were shaken for various length of time. The

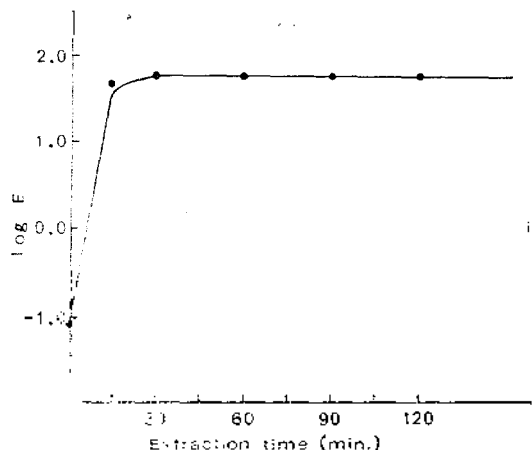


Fig. 5. Extraction of iridium(III)-tin(II) chloro complex with Alamine 336 in benzene at various extraction times. The extraction coefficient (E) was determined with Ir-192 radioactive tracer.

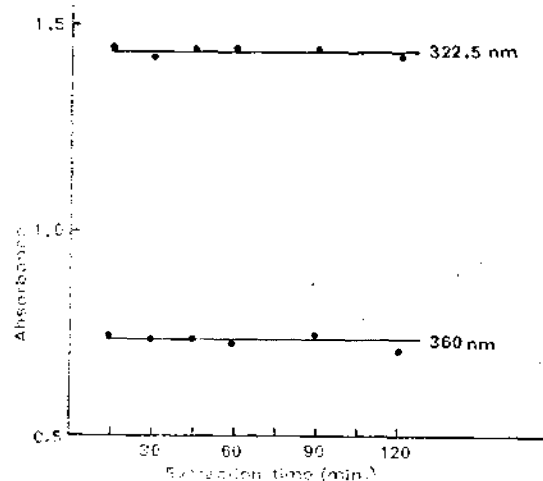


Fig. 6. The absorbance of iridium(III)-tin(II) chloro complex extracted by Alamine 336 in benzene at various extraction times.

extraction coefficients were determined using the radioactive tracer Ir-192, as shown in Fig. 5. The absorbances of amine/benzene extract were measured at 322.5 and 360 nm as shown in Fig. 6. As indicated in these two figures a shaking time of about 60 minutes was found to be adequate and was used throughout the study.

Stability, Calibration and Sensitivity. When

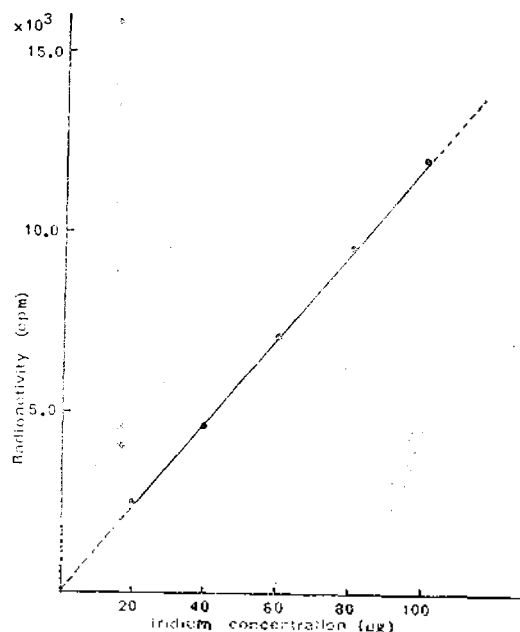


Fig. 7. The radioactivity of Ir-192 extracted in organic phase at various iridium concentrations.

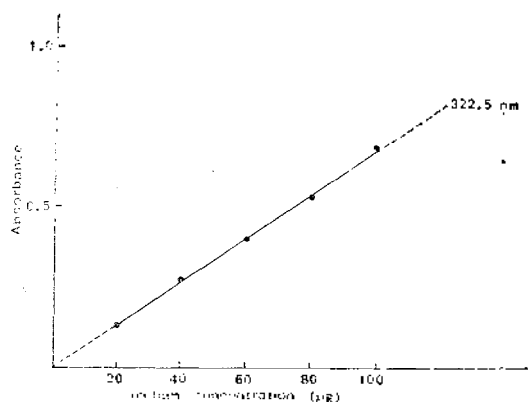


Fig. 8. The absorbance of iridium(III)-tin(II) chloro complex in organic phase at various iridium concentrations.

iridium was extracted from the aqueous solution in 1 F hydrochloric acid, the absorbance of the amine/benzene extract remained constant at least for three hours after extraction. Known concentrations of iridium, mixed with Ir-192, were extracted by the foregoing procedure and both activity (Fig. 7) and absorbance (Fig. 8) of the amine/benzene extract were measured. For solu-

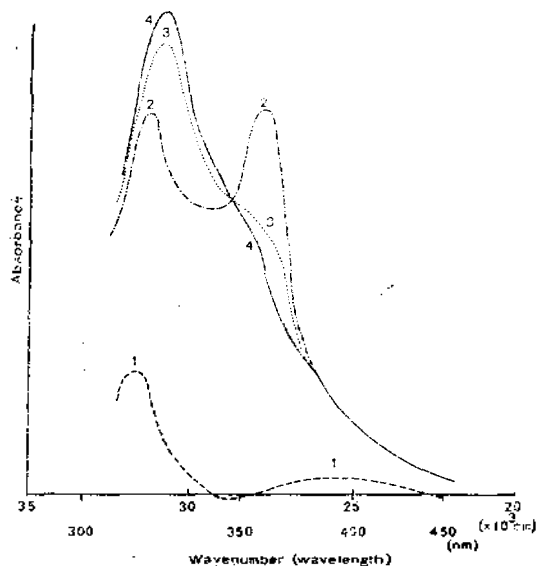


Fig. 9. The absorption spectra of iridium(III)-tin(II) chloro complex in organic phase at various warming times: 1) 0 min, 2) 15 min, 3) 30 min, 4) 90, 120 min.

tions containing between 20 and 100 $\mu\text{g}/10\text{ ml}$, Beer's law was closely obeyed (Fig. 8). An absorbance of 0.1 corresponded to approximately 15 μg Ir/10 ml when 1 cm cell was used.

Absorption Spectrum. The amine/benzene extract of iridium(III)-tin(II) complex, which was used for Fig. 3 and 4 as outlined above, was examined spectrophotometrically and the absorption curve was prepared in the range 300~530 nm (Fig. 9). The amine/benzene extract showed two absorption peaks at 316 and 395 nm when the aqueous solution was extracted without prior warming. When it was warmed for 15 minutes, two peaks approached closer occurring at 321 and 360 nm respectively. However, when warming was continued longer, i. e., 30~60 minutes, the latter peak gradually became a "shoulder" while the first peak becoming higher. When the warming time became 90~120 minutes, no more change in the absorption peak was observed and the first peak remained unshifted at 322.5 nm. It would appear, therefore, that the formation

Table 1. Interference of platinum group metals.

Iridium present, μg	Other ions, μg	Iridium found, μg
50	Pd(II), 50	50
50	Os(IV), 50	50
50	Rh(III), 50	a
50	Pt(IV), 50	a
50	Ru(III), 50	a

a: Interferences were serious, causing two to three fold increase in absorbance at 322.5 nm.

of the extractable species of colored Ir(III)-tin(II) complex is greatly affected by the length of warming time. Further, unless the extractable complex is formed, the amine/benzene does not extract iridium quantitatively as evidenced by the considerable amount of Ir-192 activity remained unextracted in aqueous phase (Fig. 3).

Interferences. The effects of other platinum group elements in the spectrophotometric determination, by the procedure outlined, were examined. Interference from rhodium(III), platinum(IV) and ruthenium(III) cannot be avoided without prior separation. No interference, however, arose from the presence of palladium and osmium as shown in Table 1.

DISCUSSION

When the amine/benzene extract, of iridium complex, yellow in color, was left being in contact with the aqueous phase, the color gradually changed to red within two days. However, if the extract was filtered through paper, the yellow color of the filtrate remained unchanged at least for several days.

As shown above, the formation of the extractable species between Ir(IV) and tin(II) was found to be critically dependent on the warming time. The species was readily extracted into the amine phase from a very wide range of hydrochloric acid concentrations. The yellow color of the amine extract was more pronounced, the

more diluted the hydrochloric acid, maximum color intensity being obtained in 1 F hydrochloric acid. From the ease with which the complex is extracted into the amine phase, it is assumed that the species are anionic and that "liquid anion exchange" occurs between the complex and the amine.

The absorption spectra of sodium hexachloroiridate in hydrochloric acid was observed, which showed two absorption peaks at 417~427.6 and 480 nm. When this complex was extracted with Alamine 336/benzene, its absorption spectra with the absorption peaks occurring at 420 and 490 nm, closely resembled that of sodium hexachloroiridate in hydrochloric acid. It is interesting to notice that such a similarity also exists between two absorption spectra, one for the stannous-chloro-complex of iridium in hydrochloric acid which shows two absorption peaks at 321 and 355 nm and the other for the amine/benzene extract of iridium(IV)-tin(II) complex having the absorption peaks at 322.5 and 360 nm. It would appear, therefore, that the yellow colored complex is extracted from aqueous solution into amine/benzene phase, probably with little change in structure.

The molar absorptivity for the stannous chloro complex of iridium in hydrochloric acid was found to be 1.8×10^4 liter cm^{-1} mole $^{-1}$ at 321 nm, which is in the same order of magnitude with the value of 3.6×10^4 liter cm^{-1} mole $^{-1}$ reported by Young.⁹

The absorption peak at 355 nm was observed as a "shoulder" as reported by the same authors.

In order to confirm that tin is extracted into organic phase as stannous-chloro-complex of iridium, the following three solutions were prepared for the qualitative test of tin in organic phases. The first and second solutions contained only stannous chloride and iridium tracers respectively. The third solution contained both

stannous chloride and iridium tracers.

After warming these solutions were extracted with amine-benzene solution as described above. Following extraction, the organic phases were rinsed with 1 M hydrochloric acid solution in order to wash free, uncomplexed tin which might have been extracted from aqueous phase. None of 1 M hydrochloric acid solutions showed the presence of tin which was confirmed by the qualitative test with mercuric chloride¹⁰ as follows. After rinsing with hydrochloric acid, mercuric chloride solution was directly added into the organic phases. Both the first and third solutions showed white precipitates of mercurous chloride indicating the presence of tin, however, the second solution showed the absence of tin.

The absorption spectrum of the organic phase was obtained for the third solution *vs.* the organic extract of the first solution. The spectrum showed the absorption peaks at 322.5 and 355 nm respectively. From these results it was concluded that stannous chloride is extracted by amine and also that stannous chloro complex of iridium is formed in aqueous solution, which is extracted into organic phase with Alamine 336.

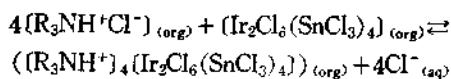
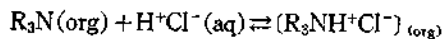
Young *et al.*⁹ also reported that the complex anion, formed between iridium(IV) and tin(II) chloride in hydrochloric acid solution, was formulated $(\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4)^{4-}$ and that on the addition of tetramethylammonium chloride to the iridium solutions the salt was formed which was formulated $(\text{Me}_4\text{N})_4(\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4)$.

They obtained the absorption peak at 326 nm with the molar absorptivity of 1.0×10^4 liter cm^{-1} mole $^{-1}$.

Although the type of amine employed in the present work was different, the molar absorptivity obtained was 1.38×10^4 liter cm^{-1} mole $^{-1}$ at 322.5 nm which is in good agreement with their value. Khattak and Magee⁴ reported that anion complex of palladium might be extracted

with tri-*n*-octylamine as $(R_3NH^+)_2PdCl(SnCl_3)_2$.

From these data as well as the present results, the extraction of iridium-tin complex may be represented by an overall reaction of the type:



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