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Short Communication

Spectrophotometric determination of platinum with iodide and rhodamine B

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Abstract

A simple and sensitive spectrophotometric method has been developed for the determination of platinum based on the ternary ion association complex with iodide and rhodamine B. The method is very sensitive ($\epsilon_{605} = 1 \cdot 2 \times 10^5$ l mole^{-1} cm^{-1}) and rapid. Interferences by various cations and anions have been evaluated.

Key words : Platinum hexaiodoplatinate, rhodamine B, spectrophotometry.

1. Introduction

Hexaiodoplatinate (IV) formed by the reaction of platinum and iodide is often used for the determination of platinum[1]. This reaction though less sensitive than *p*-nitrosodimethyl aniline[2] and *p*-aminobenzoic acid[3] has been often found useful as only palladium interferes seriously. Efforts to increase the sensitivity of this method by extraction into chloroform[4] and substituted pentanols[5] are not attractive due to combersome procedural details and low selectivity. However, the sensitivity can also be increased by the formation of a ternary complex using hexaiodoplatinate (IV) and cationic dyes as this will result in enlarged chromophore. This communication describes our studies based on this approach using rhodamine B. Similar reactions of platinum-ammonia[6], platinum-thiocyanates[7] and organic dyes have been reported in the literature.

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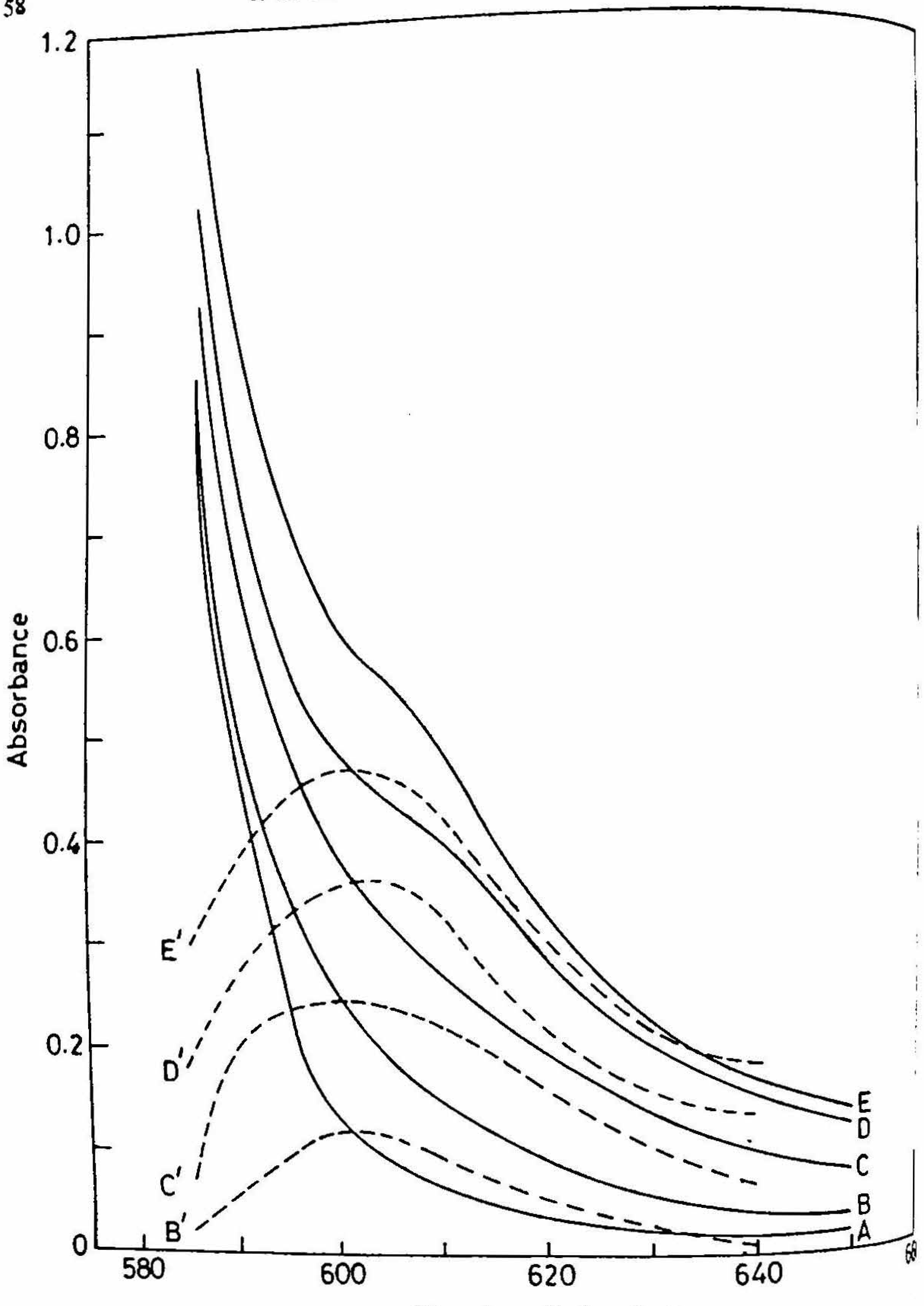


FIG. 1. Absorption spectra (Total volume 25 ml, 1 cm cells) A—5 ml of 0·02% rhodamine B, 5 m of potassium iodide and 5 ml citrate buffer. B–E as in A with the addition of 5 μg (B), 10 μg (C 15 μg (D) and 20 μg (E) of platinum. B′– D′—Absorption curves of B, C, D, E against reage Blank A.

2. Experimental

2.1. *Reagents*

Platinum (IV) solution (5 ppm) . Dissolve 1·0 g pure platinum wire in aquaregia and evaporate to dryness repeatedly by adding concentrated hydrochloric acid. Dissolve the residue in 10 ml concentrated hydrochloric acid and dilute to 1 litre, prepare a 5 ppm working solution by suitable dilution.

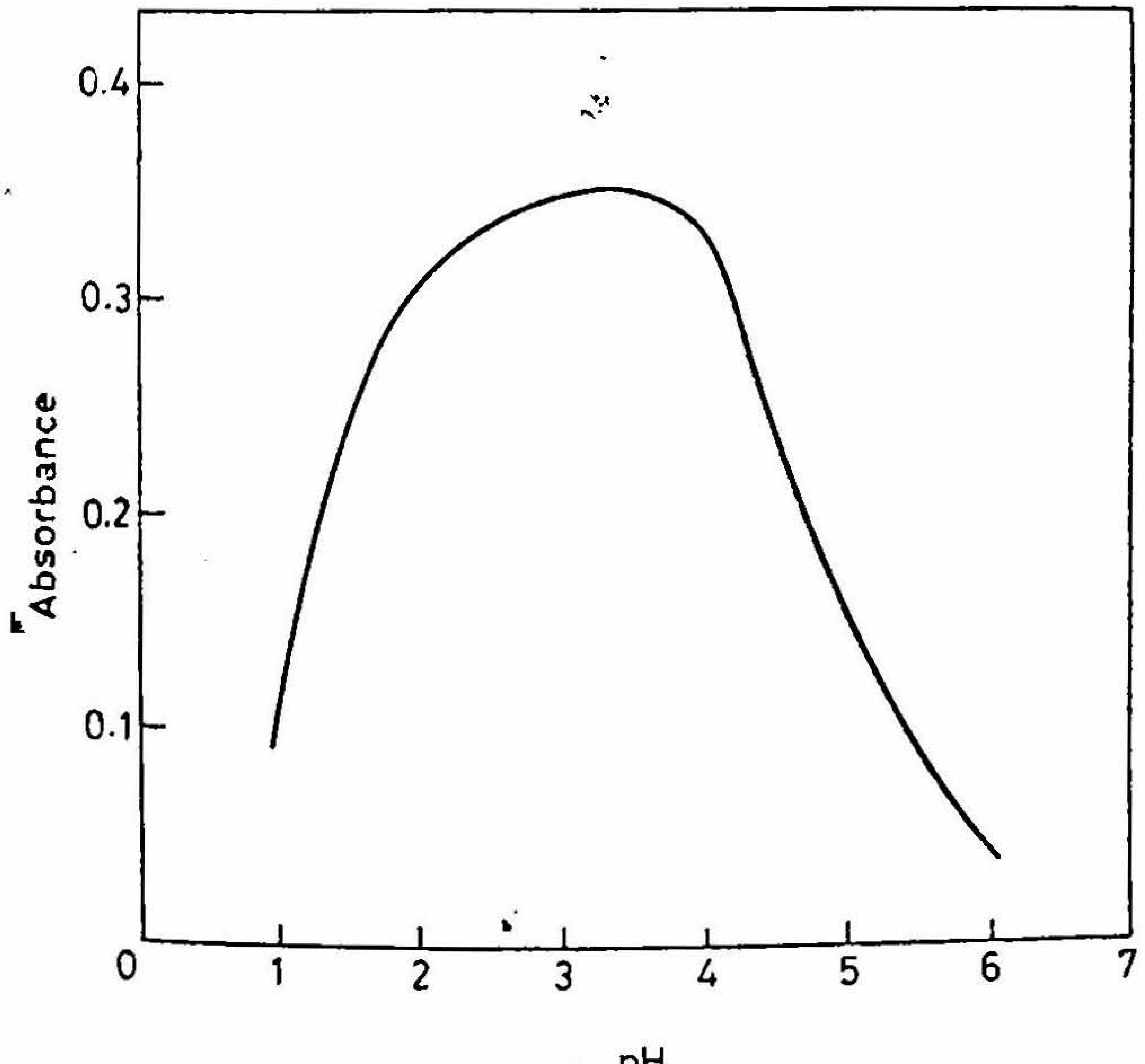
Potassium iodide solution (5%). Prepare in double distilled water.

Rhodamine B (0·02%). Dissolve 0·1 g rhodamine B in 500 ml water.

Citrate buffer (pH 3·5, 1 M). Dissolve 5·2 g citric acid in 400 ml water and adjust to pH 3·5 using sodium hydroxide and dilute to 500 ml.

2.2. *Procedure*

Transfer a sample containing not more than 30 μg of platinum (IV) into a 25 m. standard flask. Add with mixing, 5 ml of citrate buffer and 2 ml of potassium iodide



IG. 2. Optimum pH for the Pt-iodide rhodamine B reaction (Pt 15 μg, 5 ml of 2% rhodamin 2 ml of 5% potassium iodide, 5 ml citrate buffer in 25 ml, absorbance at 603 nm in 1 cm cells

Table I

Effect of experimental parameters on platinum-iodide-rhodamine B reaction

KI (5%), ml	0·2	0·4	0·8	1·2	1·6	2·0	5·0
Absorbance	0·25	0·28	0·33	0·35	0·35	0·355	0·355
Rhodamine B (0·02%), ml	0·5	1·0	2·0	3·0	4·0	8·0	10·0
Absorbance	0·25	0·28	0·33	0·35	0·35	0·355	0·35
Standing time for $[PtI_6]^{2-}$, min.	2·0	5·0	10·0	15·0	20·0	40·0	60·0
Absorbance	0·275	0·305	0·355	0·355	0·35	0·35	0·355
Inert electrolyte $NaNO_3$ (0·1 m), ml	2·0	4·0	6·0	8·0	10·0	—	—
Absorbance	0·355	0·35	0·355	0·35	0·355		

(Pt 15 µg, KI 2 ml, rhodamine B 5 ml in 25 ml except when varied.)

After 20 minutes add 5 ml of rhodamine B solution and mix thoroughly. Dilute to the mark with water and mix again. Measure the absorbance at 605 nm in 10 mm cells against a reagent blank. Establish the concentration by a calibration graph prepared for 1–30 µg of platinum using the same procedure.

3. Results and discussion

Preliminary examination of the reaction of platinum (IV), iodide and rhodamine dyes indicated that the complex precipitated on standing except in the case of rhodamine B which developed a blue colour on standing. Hence, further studies were confined to rhodamine B only. A 5 per cent solution of potassium iodide, 0·02 per cent rhodamine B solution and 15 µg platinum were employed to study this reaction.

3.1. *Absorption spectra*

Figure 1 shows the absorption spectra of the complex at different concentrations of platinum. Curves A, B–E represent the spectra of the blank and samples measured against water while B′–E′ represent the actual spectra measured against reagent blank. The complex exhibits a shoulder peak with a slight bathochromic shift at 590 nm as against 565 nm maxima of the blank. However, absorbance difference was maximum at 605 nm and this wavelength was used for analytical purposes.

Table II

Interference studies

Metal ions	Remarks
Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Be^{2+}, Bo_3^{3-}, Al^{3+}, Th^{4+}, Sn^{2+}, Po_4^{3-}, No_3^-, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, F^-, $C_2O_4^{2-}$, MOO_4^{2-} and EDTA	No interference
Cu^{2+}, Sb^{5+}, Fe^{3+}, $Cr_2O_7^{2-}$, NO_2^-, IO_3^-, ASO_4^{3-}	Interfere by oxidation of iodide to iodine
Ag^+, Tl^+, Pb^{2+}, Bi^{3+}, WO_4^{2-}	Interfere by precipitation
Cd^{2+}, Pd^{2+}, Au^{3+}, Ru^{3+}, Hg^{2+}	Interfere by forming similar complexes

3.2. *Optimization of experimental conditions*

Figure 2 shows the effect of pH on the formation of the ternary complex in the pH range 1·0 to 7·0. Maximum absorption occurs in the 3.0–3.8 pH range.

Other optimum conditions for this reaction were established by varying the desired parameters keeping others constant and these results are shown in Table I.

3.3. *Beer's law and precision*

The system obeyed Beer's law for 0–1·2 ppm of platinum in a final volume of 25 ml. The molar extinction coefficient and Sandel sensitivity were calculated to be $1 \cdot 2 \times 10^5$ $l\ mole^{-1}\ cm^{-1}$ and $0 \cdot 0017\ \mu g\ cm^{-2}$. For 10 determinations relative standard deviation was found to be 0·55%.

3.4. *Nature of the complex*

Platinum to rhodamine B ratio in the complex was found to be 1 : 2 by slope ratio, mole ratio and continuous variation methods. Since the oxidation state of platinum in the ternary complex is +4 and the ease of extraction into nonpolar solvents indicated that the complex is essentially neutral in nature with an empirical formulae of R_2PtI_6 where R represents rhodamine B molecule. Also, the fact that the complex does not show any absorption peak at 480 nm $[PtI_6]^{2-}$ and 560 nm (rhodamine B) but appears as a shoulder band with bathochromic tendency, weak bonding between amine nitrogen atom and metal ion is indicated[8]. However, since hexaiodoplatinate is coordinately saturated, R_2PtI_6 may also be regarded as an ion pair in which case the bathochromic hift of the absorption maxima can be attributed to miscellar interactions.

3.5. *Interference studies*

The recommended procedure was applied to solutions containing 15 μg of platinum and 1·5 mg of the ion. The results are summarized in Table II. The interference of Cd (II), Cu (II) and Pb (II) were overcome by the addition of 1 ml of 0.05 M EDTA. Iron and Sb (III) were effectively masked by fluoride ions. Among the noble metals only Pd (II) interfered and up to 60 μg of Pd (II) could be tolerated by first converting it to ammonia complex and then carrying out the reaction as usual. Rhodium, osmium and ruthenium did not interfere when their concentrations were maintained at 75, 45 and 15 μg respectively. Only mercury (II) and gold (III) interefered seriously. The interference of gold (III) can be eliminated using sodium nitrate or preferably oxalic acid. Mercury salts can be volatalised off if their presence is suspected. Mercury (II) and gold (III) can also be separated by Caldwell and Smiths procedure[9].

4. Conclusions

The proposed method extends the usefulness of hexaiodoplatinate (IV) reaction by the formation of ion association complex. The procedure is simple, rapid and can be modified to overcome the interferences of all the metal ions except mercury and gold. Maximum sensitivity is obtained which is equalled only by 3, 4-diaminobenzoic acid method. This method should be useful for the analysis of natural and industrial samples.

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