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Flotation Spectrophotometric Determination Of Platinum With Isochromatic Ion-Pair Between Tetrabromofluorescein And Rhodamine 6G



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ABSTRACT

The flotation spectrophotometric method for determination of platinum (Pt) with isochromatic dye ion-pair was described. [(2R6G) (PtBr₆)-3(R6G-Br)] was resolved and Rhodamine 6G (R6G) was entered into aqueous phase when pH = 5.5 HAc-NaAc buffer solution was added to the [(2R6G) (PtBr₆)-3(R6G-Br)] in medium of toluene. And then R6G-TBF was floated by tetrabromofluorescein (TBF) with toluene. The floatation was dissolved in acetone and absorbance of the solution was measured at 530 nm. The sensitivity was increased because of the assistant effect between dyes (Pt: R6G: TBF=1: 5: 5). The molar absorptivity of this method was $9.94 \times 10^5 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The concentration of Pt obeyed Beer's law in the range of 0 ~ 0.5 mg l⁻¹ with a relative standard deviation 4.4 ~ 5.8 %; the recovery of the measurement was 96.0 ~ 102.0 %. The method has been applied to the determination of platinum in platinum contained catalysts with good results.

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KEYWORDS

Platinum;
Tetrabromofluorescein;
Rhodamine 6G;
Flotation;
Spectrophotometry.

INTRODUCTION

Isochromatic dye ion-pair extraction-spectrophotometric methods for the determination of metals have been described^[1-5]. In these methods, there are some disadvantages such as the extraction rate of

the ion-pair is too low and the reagent blank value is too high. In this paper, the flotation-spectrophotometric determination of Pt with isochromatic dye ion-pair has been studied. The ion-associate was formed between the anionic bromide complex of platinum and the basic dye R6G in toluene solvent,

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which was quantitatively floated. The complex of platinum with R6G was separated and washed. Then TBF solution and acetate buffer solution of pH 5.5 were added to the Pt-Br-R6G-toluene flotation system. The platinum ion-associate was decomposed and the isochromatic dye ion-pair was formed between TBF and R6G at pH 5.5, finally the isochromatic dye ion-pair was floated by toluene again. The dye ion-pair was dissolved in acetone, the absorbance was measured at 530 nm. The separated ion-associate of Pt was considered as the formula of $[(2R6G)(PtBr)_3 \cdot 3(R6G \cdot Br)]$. The composition of isochromatic dye ion-pair was investigated, the formula is $R6G \cdot TBF$. In this method, because of assistant effect between dyes (Pt: R6G: TBF=1:5:5), the sensitivity was increased greatly. Most base metals did not affect the determination of Pt. Ir (III), Ag (I), Os and Ru (III) have tiny influence on determination.

EXPERIMENTAL

Apparatus

The absorbance was measured with a model UV-265 spectrophotometer (Shimadzu Corporation, Kyoto Japan) using 1.0 cm cells. The pH measurements were recorded with a Model PHS-3C pH meter. (Shanghai Rex Instruments Factory)

Chemicals

Platinum standard solution containing 1.00 g l^{-1} platinum was prepared by dissolving the pure metal with aqua regia. The solution was evaporated several times with concentrated hydrochloric acid and the residue was dissolved in 4.0 M hydrochloric acid. Rhodamine 6G (R6G) was used as an aqueous 1.0 mM solution; Potassium bromide was prepared for 2.5% solution; Tetrabromofluorescein (TBF) was used as an aqueous 1.0 mM solution. Acetate buffer solution of pH 5.5 was prepared by mixing 1.0 M acetic acid and 1.0 M Macetate solution. The pH of the solution was ultimately adjusted using a pH meter.

Standard procedures

To a 60 ml separatory funnel, add containing not

more than $5.0 \mu\text{g}$ of Pt, 1.0 ml of 2.0 M hydrochloric acid, 3.0 ml of 2.5% potassium bromide and 2.0 ml of 1.0 mM R6G and mix carefully, then the solution was diluted with water to 20.0 ml. The final hydrochloric acid concentration should be kept approximately 0.1M in 20.0 ml of aqueous phase. The solution was shaken with 5.0 ml toluene for about 30 s. The aqueous phase was discarded carefully. The toluene phase was washed by shaking slightly with two successive 10.0 ml portions of 0.1M hydrochloric acid for about 10 s each. The aqueous phase was discarded, 3.0 ml of 1.0 mM TBF and 2.0 ml of pH 5.5 acetate buffer solutions were added, the aqueous phase was diluted with water to 10 ml, and the solution was shaken for about 1 min. The isochromatic dye ion-pair were floated by toluene again. The aqueous phase was discarded; toluene phase and ion-pair floated were washed by shaking with two successive 10 ml portions of pH 5.5 water solutions for about 30 s each. The aqueous and the organic layers were removed carefully. The isochromatic dye ion-pair was dissolved in acetone. Then the solution was transferred to 10.0 ml volumetric flask and diluted to the mark with acetone. The absorbance of the solution was measured at 530 nm against reagent blank prepared in the same way.

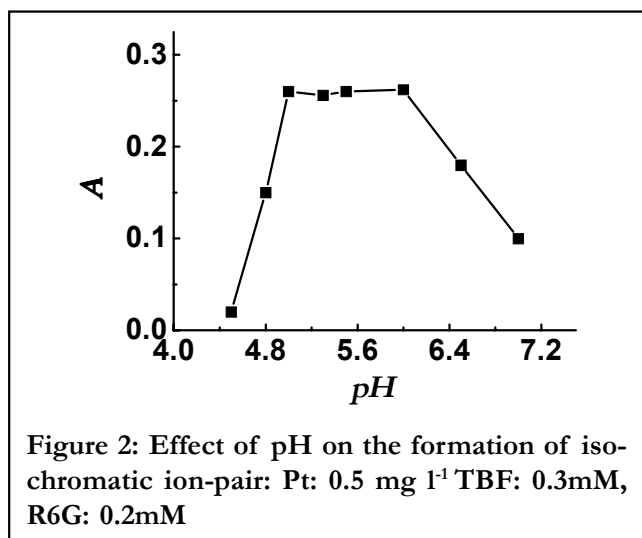
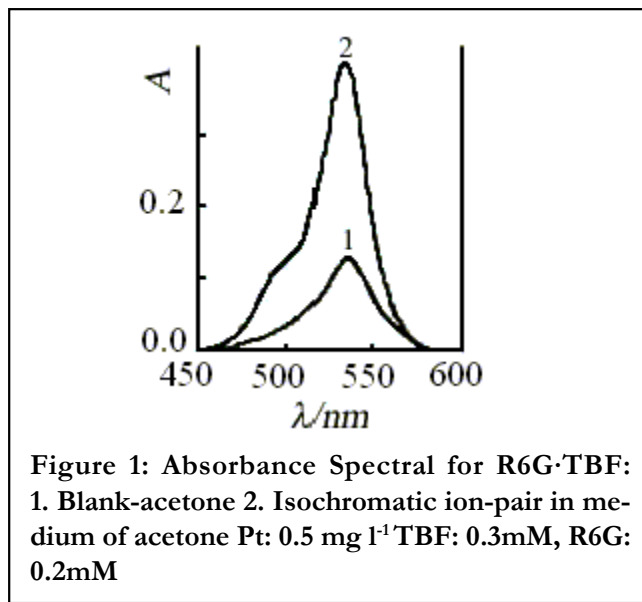
RESULTS AND DISCUSSION

The Platinum (IV) / Bromide / R6G System

The influence of the hydrochloric acid concentration on the formation and flotation of the Pt compound was studied. Maximum absorbance was obtained in the hydrochloric acid concentration range of 0.01 ~ 0.7 M. For the range of 2.0 ~ 5.0 ml bromide of 2.5 % and 1.5 ~ 4.0 ml R6G of 1.0 mM, the results were reproducible with a suitably small reagent blank, further increase in the concentration of the dye increased the value of the reagent blank.

The isochromatic dye ion-pair of R6G·TBF system

The isochromatic dye ion-pair of R6G·TBF was floated in toluene solvent. The absorbance plot of Pt was shown in figure 1. The influence of the acid-



ity on the formation and flotation of the ion-pair were shown in figure 2. Maximum absorbance was obtained in the range of pH 5.0 ~ 6.0. The concentration of TBF should be 0.05 ~ 0.5 mM. pH 5.5 solution was most suitable for washing the ion-pair. Two portions of this solution ensured that the free dye was largely removed.

Composition of the ion-pairs

Composition of the extracted Pt compound was investigated^[6]. The Pt: R6G molar ratio in the floated Pt compound was 1:5. The composition was [(2R6G)(PtBr₃)·3(R6G·Br)]. The composition of the floated isochromatic ion-pair was determined by the Jop's method of continuous variation, which revealed a

1:1 R6G to TBF. Therefore, in the proposed system the molar ratio of Pt: R6G: TBF is 1:5:5. The contrast test data was shown in TABLE 1.

TABLE 1: Contrast test data

Chromogenic System	TBF	R6G	Pt(IV)-Br-R6G System ^[6]	R6G·TBF
γ max(nm)	537	530	530	530
$\epsilon \times 10^{-5}$ (l·mol ⁻¹ ·cm ⁻¹)	0.9	1.1	4.5	9.94

* Acetone Solution

The calibration equation

According to the recommended procedure outlined above, standard calibration graphs were made. The absorbance data were processed by standard least squares treatment, and the calibration equation obtained was $\Delta A = 0.5107C$ (mg l⁻¹) + 0.0268, $R^2 = 0.9990$, where ΔA is the absorbance, C is the content of Pt and R^2 is the correlation coefficient. The concentration of Pt obeyed Beer's law in the range of 0 ~ 0.5 mg l⁻¹, the molar absorptivity of this method was 9.94×10^5 l·mol⁻¹·cm⁻¹. The precision and accuracy of the method were verified by analyzing solutions containing known amounts of Pt. The results were shown in TABLE 2.

TABLE 2: Statistical evaluation of the result of the determination of platinum with isochromatic dyes ion-pair

Platinum (μ g)		Standard deviation*	Relative standard deviation (%)	Confidence limits (probability level 0.95)
Added	Found			
1.00	1.03	0.06	5.8	1.03 ± 0.06
1.50	1.49	0.07	4.8	1.47 ± 0.07
2.00	2.04	0.09	4.4	2.05 ± 0.09

*For seven determinations

Interferences

The proposed method for the determination of Pt with isochromatic dye ion-pair is improvement from the method of determination of Pt with bromide and rhodamine 6G. This measurement has not brought interference ions. It was reported^[6] that there is no interference from 10000 times amounts of SO₄²⁻, 3000 times amounts of EDTA, Ca²⁺, Mg²⁺, NO₃⁻, Ac⁻, F⁻, 1500 times amounts of Fe³⁺, PO₄³⁻, 300 times

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amounts of Al^{3+} , Cr^{3+} , Pb^{2+} , 30 times amounts of Mn^{2+} , Be^{2+} , Sb^{5+} , W^{6+} ; 15 times amounts of Mo^{6+} , Au^{3+} , Hg^{2+} , Co^{2+} , Zn^{2+} ; 6 times amounts of Cd^{2+} , Cu^{2+} , Te^{4+} , Bi^{3+} ; 3 times amounts of Pd^{2+} , Rh^{3+} , La^{3+} , Ti^{3+} , Nb^{5+} , V^{5+} ; 2 times amounts of Ru^{3+} , Os^{4+} ; 1.5 times amounts of Ag^+ , Ir^{3+} .

ANALYTICAL APPLICATION

Determination of Pt in platinum contained catalysts

The established method was applied to the determination of Pt in Pt contained catalysts without separation. 0.10000 g of the sample was dissolved in 20.0 ml of aqua regia and evaporated until the residue was just moist. The operation was repeated after 10.0 ml of concentrated hydrochloric acid was added. The residue was heated and dissolved in 15.0 ml of 6.0 M hydrochloric acid. 20% NaOH solution was added until the light brown precipitate formed. The solution was heated in the water-bath of 50 ~ 60 °C about 20 min, then filtered, the precipitate was washed with 20 % NaOH for several times and dissolved in 5.0 ml of 6.0 M hydrochloric acid. The solution was transferred to a 100 ml volumetric flask and diluted to the mark with water. 1.0 ml of this solution was added to a separatory funnel, and then the Pt content was determined by the procedures of the proposed method. The recovery of the added platinum was in the range of 96.0 ~ 102.0 %. The platinum percent content was found to be 0.0198 %, owing to the high sensitivity of the measurement.

CONCLUSIONS

In our paper, we showed that it is possible to build high sensitive flotation-spectrophotometric methods based on the binding between an acid dye and a basic dye. The sensitivity of the proposed method is many times higher than the any previous extraction and flotation spectrophotometric methods for the determination of platinum^[6-9].

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REFERENCES

- [1] Liu Baosheng; Spectroscopy and Spectral Analysis **19(3)**, 490 (1999).
- [2] Wang Yan, Zuo Bencheng, Lihua Jianyan; Chinese Journal of Analytical Chemistry, **31(6)**, 340 (1995).
- [3] Ding Liang, Liu Baosheng, Zuo Bencheng; Chinese Journal of Spectroscopy Laboratory, **16(1)**, 47 (1999).
- [4] Zhao Xingru, Ding Liang, Liu Baosheng, Zuo Bencheng; Spectroscopy and Spectral Analysis, **19(2)**, 233 (1999).
- [5] Chen Caiping, Du Liming, Duan Yali, Zhang Yan; Chinese Journal of Analytical Chemistry, **33(2)**, 237 (2005).
- [6] Luo Daocheng, Yi Pinggui, Liu Junfeng, Shi Hongwen; Chinese Journal of Analytical Laboratory, **21(4)**, 67 (2002).
- [7] Li Lingying, Jin Gu; Chinese Journal of Analytical Chemistry, **16(5)**, 424-427 (1988).
- [8] J.R.Mudakavi et al.; J.Indian Inst.Sci., **64B(2)**, 57 (1983).
- [9] Z.Marczenko, K.Kalinowski; Anal.Chim Acta, **153**, 219 (1983).