EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM (IV) USING 2-(5- BROMO-2- OXOINDOLIN-3-YLIDENE) HYDRAZINE CARBOTHIOAMIDE AS AN ANALYTICAL REAGENT

Vasant Dnyandeo Barhate* and Parinita Umesh Madan

V.E. S. College of Arts, Science and Commerce, Sindhi Society Chembur, Mumbai 400071, India.

ABSTRACT

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of Pt(IV) by using 2-(5-Bromo-2-Oxindolin-3-ylidene)Hydrazine Carbothioamide or 5-BromoIsatin thiosemicarbazone [HBITSC] as an analytical reagent. [HBITSC] has been synthesized and characterized by elemental and spectral analysis. [HBITSC] extracts Pt (IV) quantitatively (99.67%) into n-amyl alcohol from an aqueous solution of pH range 3.0-6.0 and in the presence of 3cm³ of acetic acid-sodium acetate buffer (pH 4.6). The n-amyl alcohol extract shows an intense peak at 505 nm (λ max). Beer’s law is obeyed over the Pt(IV) concentration range of 1.0-9.0 µg/cm³. The Sandell’s sensitivity and molar absorptivity for Pt-HBITSC system is 23.07ngcm⁻² and 8452.53 L mole⁻¹cm⁻¹ respectively. The composition of extracted species is found to be 1:2 [Pt:HBITSC] by Job’s Continuous Variation and Mole Ratio Method. Interference by various ions has been studied. The proposed method is rapid, sensitive, reproducible and has been successfully applied for determination of Pt(IV) in catalyst samples.

KEYWORDS: Extractive Spectrophotometry, Pt(IV), 5-Bromo Isatin thiosemicarbazone [HBITSC], Samples.

INTRODUCTION

Platinum is one of the most important noble metal. It is mainly used as a catalyst in various chemical reactions. It is also used as a catalytic converter in automobile. It finds extensive...
use in preparing insoluble anodes, thermocouples, hard alloys, jewellery, dental and medical devices. and in chemotherapy for cancer treatment. Platinum is found in complex matrix and its concentration vary from sample to sample, therefore its determination at trace levels is very important. A solvent extraction is becoming important separation technique in chemistry. During the past two decades, considerable attention has been paid to the chemistry of Schiff bases containing nitrogen and other donor atoms and most of them are used as an efficient analytical reagent in trace analysis of some metal cations.^[1-15]^  

2-(5-Bromo-2-Oxoindolin-3-ylidene) Hydrazine Carbothioamide [HBITSC] has been used for the development of spectrophotometric method for determination of Palladium(II)[^5] and Nickie(II).[^6] In the present communication, we describe the extractive spectrophotometric determination of Pt(IV) with HBITSC.  

**MATERIAL AND METHODS**  
All the used chemicals and solvents were of AR grade and were used without further purification and all the solutions were prepared in doubly distilled water.  

ELICO - SL 159 spectrophotometer with optically matched quartz or glass cells of 1 cm path length were used for absorbance measurement. An ELICO LI-127 pH meter was employed for pH measurements.  

**Synthesis of ligand 2-(5-Bromo-2-Oxoindolin-3-ylidene) Hydrazine Carbothioamide [HBITSC]**  
Schiff base ligand HBITSC was synthesized by refluxing equimolar amount of ethanolic solution of 5-Bromoisatin with thiosemicarbazide for 4-5 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (80%, yield) which was collected by filtration. The resulting HBITSC was recrystallised using aqueous ethanol as the procedure recommended by Vogel.[^12] The product was characterized by elemental and spectral analysis.
Its solution was prepared in Dimethylformamide (DMF). A stock solution of Pt (IV) was prepared by dissolving accurately weighed platinum chloride in water containing dilute hydrochloric acid and it was standardized by stannous chloride method\[^{14}\] Working solutions of Pt (IV) were made by diluting the stock solution to an appropriate volume. All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water.

**Extractive Spectrophotometric Determination of Pt (IV)**

To an aliquot of aqueous solution containing 10-90μg of Pt(IV), 3 cm\(^3\) of acetic acid-sodium acetate buffer solution of pH 4.6 and 1ml of 0.5% solution of HBITSC prepared in DMF was added. Resulting solution was digested for 30 minutes in boiling water bath. After cooling the volume of solution was made up to 10 ml with distilled water and then equilibrated for 1 min with 10 ml of n-amyl alcohol and the phases were allowed to separate. The n-amyl alcohol extract was collected in a 10 ml measuring flask and made up to mark with n-amyl alcohol. The absorbance of n-amyl alcohol extract was measured at 505 nm against a reagent blank prepared under identical conditions. The Platinum content of the sample solution was determined from calibration curve. To study the effect of other ions, the respective foreign ions were added to aqueous phase before the extraction and adjustment of pH.

**Determination of Pt(IV) in catalyst samples**

**Procedure for Determination of Pt (IV) in Platinum-Charcoal Catalyst Sample**

0.1 to 0.2 gm. sample of Platinum catalyst was dissolved in boiling with 10 ml of aqua regia. The solution was evaporated to dryness and the residue was dissolved in 10 ml of 1M HCl filter, if required and resulting solution was diluted to 100 ml with water. 1ml aliquot of this solution was analyzed for Pt(IV) by the procedure as described earlier.

**RESULT AND DISCUSSION**

Platinum (IV) could be extracted quantitatively (99.67%) by HBITSC into n-amyl alcohol from an aqueous solution of pH 3.0 to 6.0. (Fig.1) Organic solvents used for extraction of Pt(IV) can be arranged on the basis of their extraction coefficient values as n-amyl alcohol > n-butanol > ethyl acetate > benzyl alcohol > chloroform > carbon tetrachloride > xylene > nitrobenzene > toluene > chlorobenzene (Fig.2). n-amyl alcohol was found to be the best extracting solvent; hence, it was selected for extraction throughout the work. The n-amyl alcohol extract of Pt- HBITSC complex showed intense peak at 505 nm. (Fig.3). The absorbance due to the reagent is negligible at this wavelength, so the absorption measurements were taken at this wavelength. The result shows that the system confirmed to
Beer’s law at this wavelength over a platinum (IV) concentration range 1.0 to 9.0 μg/cm$^3$ (Fig4). The molar absorptivity of the extracted complex on the basis of Pt(IV) content was calculated to be 8452.53 L mol$^{-1}$ cm$^{-1}$. The Sandell’s sensitivity was found to be 23.07 ng/cm$^2$. It was found that 1 ml of 0.5% DMF solution of HBITSC was sufficient to extract 90 μg of Pt (IV). (Fig5). The colour of the n-amyl alcohol extract was found to be stable at least 48 hrs at room temperature. (Fig6).
Fig. 3. Solution A: Absorbance spectra of HBITSC.
Solution B: Absorbance spectra of Pt – HBITSC Complex

Fig. 4 Calibration curve for Pt(IV).

Fig. 5: Absorbance of Pt: HBITSC into n-amyl alcohol as a function of time.
Effect of other ions

Pt(IV) (60µg) was determined in the presence of various ions. The following ions in the amount indicated, did not interfere in the spectrophotometric determination of Pt(IV)(60µg):

a) 10 mg each of Li(I), Ca(II), Mg(II), Al(III), Ba(II), Sr(II), Pb(II), Sn(II), Be(II), W(VI), Mo(VI), U(VI), V(V).

b) 5mg each of Zn (II), Hg (II), Ag(I), As(III), Bi(III) and Sb(III).

c) 2mg each of Mn (II) and Cd(II).

d) 1mg each of Ce(IV), Th(IV) and Zr(IV).

e) 0.5mg each of Fe(II), Fe(III) and Ni(II).

f) 0.1 mg each of Co(II), Cu(II), Cr(III), Ru(III), Ir(IV), Os(IV) and Pd(II).

g) 20 mg each of - chloride, bromide, fluoride, sulphate, persulphate, nitrate, phosphate, acetate, oxalate, citrate and tartarate. Interference due to iodide, nitrite and thiosulphate and EDTA was removed by boiling solution with concentrated HNO₃ before the adjustment of pH.

Composition of the Extracted Complex

The composition of the extracted complex was found to be 1:2 Pt(IV) (Pt: HBITSC) by Job’s continuous variation and Mole ratio method(Fig-6 & 7).

![Composition of extracted species[Pt: HBITSC] by Job’s Continuous variation method.](image-url)
Precision, Accuracy, Sensitivity and Application of Method

The precision and accuracy of the method were tested by analyzing the solution containing a known amount of Pt(IV) following the recommended procedure. The average of 10 determination of 30 μg of Pt (IV) in 10 cm³ solutions was 30.15μg, which is varied between 29.908 μg and 30.392μg at 95% confidence limit. Standard deviation and Sandell’s sensitivity of the extracted species is found to be 0.338 and 23.07ng cm⁻² respectively. The sensitivity of the method is comparable with those of the existing methods for the determination of Pt(IV). (Table-1)

Table 1.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Sandell’s Sensitivity ng cm⁻²</th>
<th>Molar Absorbtivity L mol⁻¹ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicyaldehyde thiosemicarbazone</td>
<td>30</td>
<td>6500</td>
</tr>
<tr>
<td>Benzyl - a – oxime</td>
<td>29.30</td>
<td>6670</td>
</tr>
<tr>
<td>Potassium butyl xanthate</td>
<td>48.8</td>
<td>4002</td>
</tr>
<tr>
<td>1- (2-pyridyl)-4,4,6-trimethyl IH, 4H - pyrimidine - 2- thiol</td>
<td>39</td>
<td>5000</td>
</tr>
<tr>
<td>Isonitroso thiocamphor</td>
<td>23.8</td>
<td>8200</td>
</tr>
</tbody>
</table>

Thus it is obvious that the method developed offers some distinct advantage over existing methods particularly with respect to sensitivity and molar absorptivity for complex formation. The proposed method has been applied for the determination of Pt (IV) in catalyst samples. The results of the analysis of the samples were comparable with certified values and stannous chloride method[14] (Table-2).
Table 2. Determination of Pt(IV) in catalyst sample

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pt (IV) found %</th>
<th>Pt(IV) found %*</th>
<th>Certified value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt charcoal catalyst (Parekh platinum Ltd.)</td>
<td>1.05</td>
<td>1.06</td>
<td>1.00</td>
</tr>
<tr>
<td>Pt charcoal catalyst (Hindustan platinum Ltd.)</td>
<td>0.99</td>
<td>1.05</td>
<td>1.00</td>
</tr>
</tbody>
</table>

* Average of three determinations.

ACKNOWLEDGEMENT

Authors are thankful to the Principal Dr. (Mrs.) J. K. Phadnis, V.E. S. College of Art, Science and Commerce, Sindhi Society, Chembur Mumbai - 71 for providing necessary research facilities.

REFERENCES

1. Shelar SY, Bhor RJ, Anuse MA, NavalRM. (Separation and Spectrophotometric Determination of Osmium(IV) and Ruthenium(III) with O-methoxyphenyl Thiourea as Chromogenic Legand: Sequential Separation of Osmium(IV), Ruthenium(III), and Platinum(IV) ). Separation Science and Technology, 2015; 50(8): 1190-1191.