Highly selective first order derivative spectrophotometric determination of osmium(VIII) using anthranilic acid as a chromogenic reagent

Louis George, Anitha Varghese* & Rajani Kulkarni
Department of Chemistry, Christ University, Bangalore 560 029, India.
E-mail: anitha.varghese@christuniversity.in

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A simple, selective and sensitive spectrophotometric method has been developed for the determination of osmium(VIII) using anthranilic acid as a reagent in the presence of Triton X-100. The molar absorptivity and Sandell’s sensitivity of the violet coloured species are $3.03 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ and 3.5 ng cm$^{-2}$ respectively. Beer’s law is obeyed between 0.5-5.5 $\mu$g mL$^{-1}$ of Os(VIII) at 500 nm. The stoichiometry of the complex is found to be 1:2 (metal: ligand). Calibration graph for the first order derivative spectrophotometric determination of Os(VIII) is derived by measuring derivative amplitudes at 525 nm with a linear range 0.25-5.5 $\mu$g mL$^{-1}$. The detection limit and quantitation limit of first order derivative spectrophotometry are found to be 0.075 and 0.25 $\mu$g mL$^{-1}$, respectively. The metal ions, which are normally associated with osmium in catalysts and alloy samples, do not interfere. The proposed method has been successfully applied for the trace level determination of osmium in various synthetic mixtures containing commonly associated metal ions and corresponding to the alloy composition.

Keywords: Osmium(VIII), Anthranilic acid, Derivative spectrophotometry, Alloys

The renewed interest in the chemistry of osmium stems from their fascinating electron-transfer, photochemical and catalytic properties exhibited by the complexes of this metal. Alloys containing osmium possess unique physical chemical properties, especially refractoriness in combination with high corrosion resistance and high conductivity$^1$. For these reasons these alloys have wide practical applications in modern technology such as hard coatings of cutting tools and abrasives, hydrogenation catalysts, electrochemical reactor devices, heavy-fermion superconductor and biocompatible substrates$^{2,3}$. Osmium tetroxide is an efficient catalyst for olefin hydroxylation and dihydroxylation reactions$^{4,6}$. Various osmium complexes have been reported as catalysts for olefin metathesis, microenzyme sensors and electroluminescent materials$^{7,9}$. Survey of literature reveals that several analytical techniques have been reported for the determination of osmium in various samples such as high performance liquid chromatography$^{10,11}$, inductively coupled plasma atomic emission spectroscopy$^{12}$, spectrofluorometry$^{13}$, atomic absorption spectrometry$^{14}$, flame atomic emission spectrometry$^{15}$ and spectrophotometry$^{16-20}$. Simplicity, less expensive instrumentation and high sensitivity make spectrophotometric methods superior to other analytical techniques. A number of chromogenic reagents such as 5-chloro-2-hydroxythiobenzhydrazide$^{21}$, promazinehydrochloride$^{22}$, ethylene thiourea$^{23}$, Brilliant green$^{24}$, pyrocatechol and hydroxyamidine$^{25}$ have been reported for the determination of osmium at trace levels.

Most of the reported methods suffer from a number of limitations such as lack of sensitivity$^{16,17}$, require tedious and time consuming extraction, heating or lack of selectivity$^{21-25}$. 5-chloro2-hydroxythiobenzhydrazide is a sensitive reagent for the determination of osmium but the method involves extraction of complex into microcrystalline naphthalene followed by dissolution into chloroform, which is a hazardous chemical. The method also suffers serious interference from associated metal ions and masking by suitable reagents is required$^{21}$. The reagent pyrogallol red suffers from interference by many metal ions; osmium requires prior separation by extraction into methyl ketone and back extraction into sodium hydroxide solution which increases the time of determination$^{27}$. However in the present method the use of micellar system enables the measurements in an aqueous medium there by avoiding the extraction steps, while the derivatisation of the spectral profiles enhances the selectivity of the method as closely overlapped absorption bands of the interfering ions become resolved$^{26}$. 
In the present investigation we report a simple, selective and non-extractive derivative spectrophotometric determination of osmium(VIII) using anthranilic acid (AA) in presence of Triton X-100, a neutral micellar medium. The distinct advantage of the proposed method is that the commonly associated metal ions especially Pt, Pd, Ru and Cu could be tolerated in considerable excess unlike the reported methods. Osmium is found in nature as an alloy, mostly in platinum ores. It was identified in a black residue remaining after dissolving platinum ore with aqua regia. Osmium is also used in alloys with platinum, iridium and other platinum group metals. Those alloys are employed in fountain pen tips, electrical contacts and in other applications where extreme durability and hardness are needed. Therefore it is of great interest to determine osmium in the presence of platinum. A derivative spectrophotometric method of selective determination of Os(VIII) in the presence of Pt(IV) without any pre-separation is also reported. Impact of varying parameters such as effect of acids, concentration of surfactant and reagents on the absorbance and the stability of the complex have been studied. The developed procedure has been successfully applied for the determination of osmium in synthetic mixtures of some alloy samples.

### Experimental Section

#### Apparatus

A Shimadzu 1800 UV/VIS spectrophotometer equipped with 1.0 cm quartz cells was used for all spectral measurements. The instrumental parameters were optimised and the best results were obtained with a scan speed 370 nm/min, slit width of 1 nm and $\Delta \lambda = 2$ nm for the first order derivative mode in the wavelength range 350-650 nm. A Systronics $\mu$ pH system 362 was used for pH measurements.

#### Reagents and solutions

A standard solution of osmium was prepared by dissolving 1 g of osmium tetraoxide (s. d. fine-chem. Ltd. India) from a sealed ampoule in 50 mL of 0.2 M sodium hydroxide solution and made up to the mark in a 100 mL volumetric flask with doubly distilled water. The solution was standardized iodometrically and working solutions were prepared by diluting the stock solution. A 0.1% solution of AA (s. d. fine-chem. Ltd. India) was prepared in ethanol. Sodium acetate acetic acid buffer of pH 4.5 was prepared by mixing appropriate volumes of 0.2 M each of sodium acetate and acetic acid. Solutions of the studied interfering ions of suitable concentrations were prepared using A.R. grade reagents. 1% Triton X-100 was prepared (CDH Pvt. Ltd. India.) in distilled water.

### Results and Discussion

Anthranilic acid reacts with Os(VIII) instantaneously at room temperature to form intense violet coloured species having maximum absorbance at 500 nm where the reagent blank showed negligible absorbance. The optimum reaction conditions for the quantitative determination of Os(VIII) was established from the preliminary studies.

#### Effect of pH

Less intense coloured species were formed in various acids such as sulphuric, hydrochloric, nitric and phosphoric acid. Acetic acid medium was also found to be not effective. The coloured species formed in basic buffers were found to be more intense but many metal ions interfered seriously in the determination. Of the various acidic buffers studied, sodium acetate-acetic acid buffer solution of pH 4.5 was found to be the best for the system. The absorbance was found to be maximum and constant in the pH range 4.8-6.04. Hence 3 mL of sodium acetate-acetic acid buffer solution of pH 4.5 was used for this analytical work.
Effect of surfactants

The effect of various surfactants such as Triton X-100 (neutral surfactant), sodium lauryl sulphate, SLS (anionic surfactant), cetylpyridinium chloride, CPC and cetyldimethylammonium bromide, CTMB (cationic surfactants) on the absorption profiles of each system has been investigated. It was observed that addition of Triton X-100 was accompanied by solubilising and sensitising the coloured species. On the other hand a comparatively low absorbance was observed with the addition of CPC, CTMB or SLS. In the presence of Triton X-100 the chelates exhibited maximum molar absorptivity (Table 1). Consequently Triton X-100 has been selected to improve the sensitivity and stability of the coloured species. 1.0 mL of 1% Triton X-100 was found to be optimum for this analytical work.

Effect of reagent concentration

The effect of concentration of the reagent on the absorption profiles of the system has been investigated in normal mode. Varying amounts of AA were added to a fixed concentration of Os(VIII) and the absorbances were measured according to the standard procedure. A volume of 2.0 mL of 0.1% AA in a total volume of 10.0 mL was found to be optimum for determinations of osmium (up to 55.0 µg) in micellar medium. It was noticed that an excess of reagent had no effect on sensitivity or stability of the complexes. The absorbances of the complexes were found to remain constant at least for 6 h at room temperature, which showed that these coloured species are stable.

Calibration graphs and analytical parameters

Beer’s law is obeyed in the concentration range 0.50-5.50 µg mL⁻¹. The molar absorptivity and Sandell’s sensitivity values of osmium-AA species calculated from Beer’s law data are $3.03 \times 10^4$ L mol⁻¹ cm⁻¹ and 3.5 ng cm⁻² respectively. The linear regression analysis of absorbance, $[A]$ at $\lambda_{\text{max}}$ of the complex versus metal ion concentrations (µg mL⁻¹), shows a good linear fit (Table 2).

First order derivative spectra of osmium-AA complex shows a peak at 470 nm, a trough at 525 nm and a cross over point at 500 nm, corresponding to the $\lambda_{\text{max}}$ of the complex (Fig. 1). The derivative amplitudes measured at 470 nm and 525 nm were found to be proportional to the concentration of Os(VIII). The linear regression analysis of the change in derivative amplitude versus the analyte concentration shows a good linear fit. The characteristics of calibration graphs are given in Table 2. Based on the better sensitivity and selectivity, determination of osmium(VIII) by first derivative spectrophotometry is recommended at 525 nm. A linear plot was obtained in the concentration range 0.25-5.5 µg mL⁻¹ of Os(VIII). The high value of correlation coefficient and closeness of the intercept to zero show that calibration graphs are linear and obey Beer’s law. Limit of detection $C_L$ (k=3) and limit of quantification $C_Q$ (k=10) in normal and derivative modes are reported in Table 2. The limit of quantification, $C_Q$ is used to determine the lower limit of linear range²⁸.

Stoichiometry and probable structure of the complex

The stoichiometry of the complex was investigated by Job’s continuous variation method and mole ratio method and was found to be 1:2 (metal: ligand). The stability constant of complex was determined by limiting logarithmic method²⁹ and was found to be $2.56 \times 10^5$. The nature of the species was investigated by passing an aliquot of the solution through a cation (Amberlite IR 120) and an anion (Amberlite IRA 400) exchange resin. Only cation exchange resin retained the coloured species, indicating the cationic nature of the species.

### Table 1 — Influence of different surfactants on the absorbance of Osmium-AA species

<table>
<thead>
<tr>
<th>Surfactant(0.1)%</th>
<th>Type</th>
<th>$\lambda$(nm)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
<td>500</td>
<td>0.345</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>Neutral</td>
<td>500</td>
<td>0.359</td>
</tr>
<tr>
<td>CPC</td>
<td>Cationic</td>
<td>505</td>
<td>0.347</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cationic</td>
<td>505</td>
<td>0.340</td>
</tr>
<tr>
<td>SLS</td>
<td>Anionic</td>
<td>495</td>
<td>0.342</td>
</tr>
</tbody>
</table>

Condition: [Os(VIII)] = 3.0 µgmL⁻¹; 2.0 mL of 0.1% AA; 3 mL buffer solution of pH 4.5.

### Table 2 — Analytical parameters of Osmium-AA complex

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Normal 500 nm</th>
<th>First derivative 470 nm</th>
<th>525 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit</td>
<td>1.50×10⁻¹</td>
<td>1.05×10⁻¹</td>
<td>7.50×10⁻²</td>
</tr>
<tr>
<td>Quantitation limit</td>
<td>5.01×10⁻¹</td>
<td>3.50×10⁻¹</td>
<td>2.5×10⁻¹</td>
</tr>
<tr>
<td>Linear range</td>
<td>0.50-5.5</td>
<td>0.35-5.5</td>
<td>0.25-5.5</td>
</tr>
<tr>
<td>Regression equation (y)⁹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope (m)</td>
<td>1.12×10⁻¹</td>
<td>5.90×10⁻³</td>
<td>1.05×10⁻²</td>
</tr>
<tr>
<td>Intercept (c)</td>
<td>-1×10⁻³</td>
<td>3.0×10⁻⁴</td>
<td>2.0×10⁻⁴</td>
</tr>
<tr>
<td>Correlation coefficient (r)</td>
<td>0.9997</td>
<td>0.9990</td>
<td>0.9998</td>
</tr>
<tr>
<td>Relative standard deviation (%)</td>
<td>0.96</td>
<td>0.77</td>
<td>0.93</td>
</tr>
</tbody>
</table>

⁹$y = mx + c$ where y, absorbance/derivative amplitudes; m, slope; x, concentration of osmium(VIII) in µg mL⁻¹; c, intercept.

²⁸Recommended for estimation
In order to understand the nature of bonding attempts have been made to isolate the coloured species from the solution phase by extraction into ethyl acetate in the absence of Triton X-100. The extract on slow evaporation yielded a solid product. The reagents were found to be not soluble in the solvent. Characterisation of isolated species was done by elemental analysis (Calcd: C, 33.87; H, 2.84; N, 5.64; O, 19.33; Os, 38.31%. Found: C, 33.28; H, 2.54; N, 5.92; O, 19.45; Os, 38.76%) and IR spectral analysis. In the IR spectrum of complex ν\text{C=O} band remains in the original position (1690 cm\(^{-1}\)) as in the free ligand demonstrating non-involvement of this group in coordination. The bands due to –NH and –OH, merged and shifted to lower frequencies (3170-3300) compared to free ligand values indicating bonding through nitrogen and oxygen atoms. A band characteristic of OsO\(_4\) is observed at 890 cm\(^{-1}\).

OsO\(_4\) exists as the perosmate ion, [OsO\(_4\)(OH)\(_2\)]\(^2-\) in an alkaline solution\(^2\). But in an alcoholic solution of the reagent it forms osmate ion [OsO\(_2\)(OH)\(_4\)]\(^2-\) by reaction with alcohol and forms osmyl complex by the replacement of hydroxyl groups with donor atoms of the ligand. The probable structure of the coloured species and its optimised geometry are proposed in Figs. 2 and 3.

Effect of diverse ions

To assess the usefulness of the proposed method the effect of diverse ions on the trace level determination of osmium (2.5 μg mL\(^{-1}\)) has been investigated in normal and in first derivative modes. The tolerance limit was taken to be the amount that caused a ±3% change in absorbance. The tolerance limits of the foreign ions tested are given in Table 3. Alkali and alkaline earth metal ions and a large number of anions did not interfere even when present in large excess. Cations like Ru(III), Pd(II), Rh(III) and Pb(II) which are usually associated with osmium containing samples did not interfere in both zero order and derivative modes. The most serious interference was from Pt(IV) ions due to the complex formation

<table>
<thead>
<tr>
<th>Ions</th>
<th>Tolerance limit (μg mL(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride, bromide, nitrate, phosphate, sulphate, fluoride, oxalate, acetate</td>
<td>&lt; 4500</td>
</tr>
<tr>
<td>Na(I), K(I), Mg(II), Ba(II), Ca(II), Sr(II), Al(III)</td>
<td>≤ 900</td>
</tr>
<tr>
<td>Co(II), Ni(II), Mn(II), Zn(II), Cd(II), Pb(II), Bi(III), Fe(III), Ti(IV)</td>
<td>≤500</td>
</tr>
<tr>
<td>Cu(II), Zr(IV), Zn(II), Ag(I), Pd(II)</td>
<td>100</td>
</tr>
<tr>
<td>Mo(VI), Ru(III), Rh(III)</td>
<td>50</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>2 (30)(^a)</td>
</tr>
</tbody>
</table>

\(^a\)Measurement in the derivative mode at 470 nm.
Table 4 — Comparative evaluation of various spectrophotometric reagents for the determination of osmium

<table>
<thead>
<tr>
<th>Reagents</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon \times 10^4$ (L mol$^{-1}$ cm$^{-1}$)</th>
<th>Beer’s law limits (µg mL$^{-1}$)</th>
<th>Remarks</th>
<th>Ref No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylisobutrazine hydrochloride</td>
<td>519</td>
<td>2.4</td>
<td>0.25-7.50</td>
<td>Many interferences, Multiple extraction</td>
<td>18</td>
</tr>
<tr>
<td>Ethylene thiourea</td>
<td>490</td>
<td>16.8</td>
<td>0.03-3</td>
<td>Many interferences</td>
<td>23</td>
</tr>
<tr>
<td>Oxidation of carminic acid by $\text{H}_2\text{O}_2$</td>
<td>540</td>
<td>--</td>
<td>0.1-1.5</td>
<td>Highly basic medium is used. Multiple extraction is needed to remove interference</td>
<td>16</td>
</tr>
<tr>
<td>Pyrogallol red-bromate reaction</td>
<td>545</td>
<td>--</td>
<td>0-1.4</td>
<td>Very short time limit, Multiple extraction</td>
<td>17</td>
</tr>
<tr>
<td>2,4-Dimethoxybenzaldehyde</td>
<td>510</td>
<td>1.05</td>
<td>1.8-14.4</td>
<td>Coprecipitation on microcrystalline naphthalene</td>
<td>21</td>
</tr>
<tr>
<td>Isonicotinoyl hydrazone</td>
<td>423</td>
<td>1.6</td>
<td>--</td>
<td>Required heating at 75°C for 15 min.</td>
<td>30</td>
</tr>
<tr>
<td>Quercetin</td>
<td>560</td>
<td>1.6</td>
<td>0.5-11.4</td>
<td>Method is based on oxidation of iodide</td>
<td>31</td>
</tr>
<tr>
<td>2-(4-Diethylaminostyryl)-1,3,3-trimethyl-6-nitro-3$H$-indolium chloride</td>
<td>525</td>
<td>3.03</td>
<td>0.5-5.5</td>
<td>Selectivity is enhanced by derivative mode without any pre-separation or use of masking agents</td>
<td>Present work</td>
</tr>
</tbody>
</table>

with AA. The interference due to the presence of Pt(IV) ions in the determination of osmium could be overcome by using the derivative mode. The measurement in the first derivative mode at 470 nm (zero-crossing point of platinum-AA complex) increases the tolerance limit of Pt(IV) up to 12-fold excess. Thus the selectivity of the method is considerably enhanced by recording spectra in the derivative mode without any pre-separation or addition of masking agents. A comparative evaluation of the present method with various other reported methods is given in Table 4.

**Determination of Os(VIII) in presence of Pt(IV) using first order derivative spectrophotometry**

Pt(IV) forms coloured species on interaction with AA having maximum absorbance at 470 nm. The intensity of platinum-AA coloured species under the optimum conditions of osmium-AA complex was found to be very low. The determination Os(VIII) in presence of Pt(IV) by conventional spectrophotometry was difficult since the spectral profiles of these species in zero order modes overlap with each other significantly. The selectivity of the method is considerably enhanced by recording spectra in the derivative mode in which closely overlapped absorption profiles in the normal mode of the analyte (Os(VIII)) and the interfering ions (Pt(IV)) get resolved into separate peaks, troughs and cross-over points as shown in Fig. 4.

![Fig. 4 — First order derivative spectra of osmium-AA and platinum-AA complexes.](image)

The derivative amplitudes measured at 470 nm (zero crossing point of platinum-AA complex) were found to be independent of concentration of platinum(IV). This was confirmed by the construction of calibration graphs for the standards containing Os(VIII) alone and in the presence of Pt(IV) ions at 470 nm.

The linear regression analysis of the change in derivative amplitudes versus the analyte concentration
gives the following equations. Correlation coefficient values are given in parenthesis.

\[
[PH]_{470 \text{ nm}} = 5.90 \times 10^{-3} [\text{Os(VIII)}] + 3.0 \times 10^{-4} (0.9990) \quad \ldots (1)
\]

\[
[PH]_{470 \text{ nm}} = 5.87 \times 10^{-3} [\text{Os(VIII)}] + 3.8 \times 10^{-4} (0.9995) \quad \ldots (2)
\]

The slopes of the calibration graphs had similar values implying that the interference of platinum(IV) is completely removed. Thus by measuring the derivative amplitudes at 470 nm the interference due to platinum(IV) ions can be eliminated up to 10-fold excess without any pre-separation or addition of masking agents.

### Applications of the method

**Analysis of osmium in synthetic mixtures**

As compared to the cost of platinum group metals, this working place cannot afford to purchase real samples containing osmium. The applicability of the method was tested by analyzing synthetic samples containing added osmium. Synthetic samples were prepared by mixing microgram amounts of Os(VIII) with other metal ions in suitable proportions. The obtained results are in good agreement with the amount of metal ion initially added as shown in Table 5. The low relative standard deviation values for analysis of five replicates indicated good precision of the proposed methods. The recovery of the metal was found to be greater than 99%. The validity of the proposed method was determined in several synthetic binary mixtures containing Os(VIII) and Pt(IV). Satisfactory results were obtained for the recovery of osmium indicating that the proposed method is effective for the determination of osmium in presence of platinum. The results are given in Table 6. Thus the proposed method can be successfully applied for estimating osmium at the microgram level from its ore sample and alloy samples.

### Conclusion

The proposed method permits the determination of trace level amounts of Os(VIII) in presence of platinum without any prior separation. The major advantage of the proposed method is that colour development is instantaneous at room temperature without the need for heating or extraction. First derivative mode is found to be more precise, sensitive and selective. The proposed method can be used as an alternative method for the determination of trace amounts of osmium in various alloys as the associated metal ions in these materials do not interfere with the determination.

### References