



Synthesis, Structural Characterization and Spectrophotometric Determination of Ruthenium (VI) in Presence of Micellar Medium Using 4-Hydroxy-3, 5-Dimethoxy Benzaldehyde 4-Hydroxy Benzoylhydrazone

KEYWORDS

Ruthenium (VI), Spectrophotometry, HDMBHBH, Micellar medium, C-TAB.

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ABSTRACT A rapid, simple, sensitive and selective Spectrophotometric method has been developed for the determination of Ruthenium (VI) using 4-Hydroxy 3, 5-dimethoxy benzaldehyde 4-hydroxy benzoylhydrazone (HDMBHBH). Ruthenium (VI) forms a light pink coloured water-soluble complex with HDMBHBH in presence of C-TAB (5%) and the complex shows maximum absorbance while the reagent blank shows negligible absorbance at λ_{max} 420 nm and at pH 5.5. Beer's law was obeyed in the range 0.202-2.022 mg/mL and the optimum concentration range from ringbom plot was 0.404-1.819 mg/mL of Ruthenium (VI). The molar absorptivity and Sandell's sensitivity for the coloured solution were found to be $3.00 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0033 \text{ } \mu\text{g} \cdot \text{cm}^{-2}$ respectively. The interference effect of various diverse ions has been studied. The complex shows 1:1 [Ru (VI): HDMBHBH] stoichiometry with stability constant 3.4×10^6 . The standard deviation of the method in the determination of $1.011 \text{ } \mu\text{g ml}^{-1}$ of Ruthenium (VI) was 0.002. First and second order derivative spectrophotometric methods were developed at λ_{max} 440 nm and 460 nm respectively for the determination of Ruthenium (VI), which was more sensitive than the zero order method. The developed method has been used for the determination of Ruthenium (VI) in environmental water and alloy samples.

Introduction:

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al [1]. Hydrazones are important class of known analytical reagents. Derivative spectrophotometry was a very useful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences. Hydrazones and its derivatives reacts with many metal ions forming colour complexes and act as chelating agents. A micellar solution has the ability to enhance the stability of metal complex and has been utilized as a medium for the spectrophotometric determination of the metal chelate [2-4].

Ruthenium is a hard white metal. It does not transit at room temperatures, but oxidizes explosively at high temperatures. The metal is not attacked by hot or cold acids or aqua-regia. The oxidation states of ruthenium range from +1 to +8. The chief source of Ruthenium is Osmiridium in which it ranges from 0.2% to about 20%. Ruthenium has highly effective ability to harden platinum, palladium and it is alloyed with these metals to make electrical contacts for severe wear resistance. The corrosion resistance of titanium is improved a hundred fold by addition of 0.1% ruthenium.

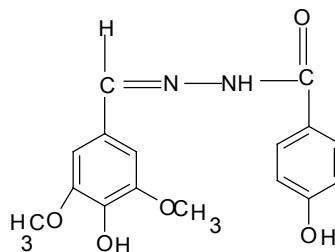
Experimental part: materials and methods:

The reagent (HDMBHBH) was prepared by the Sah and Daniels [5] procedure. After recrystallisation of the crude product HDMBHBH was appeared in the light greenish coloured crystals. The molecular structure of HDMBHBH ($\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_5$) was confirmed based upon IR, NMR and Mass spectral data. Melting point of HDMBHBH was found to be 292-294°C.

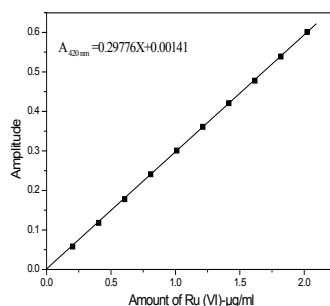
The absorbance and pH measurements were made on a Shimadzu UV-Visible Spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy was 0.5 nm with automatic wavelength correction and the recorder was a computer controlled thermal graphic printer with a cathode ray tube and one degree of freedom in the wavelength range 300-800 nm.

Results and discussion: The chromogenic reagent 4-Hy-

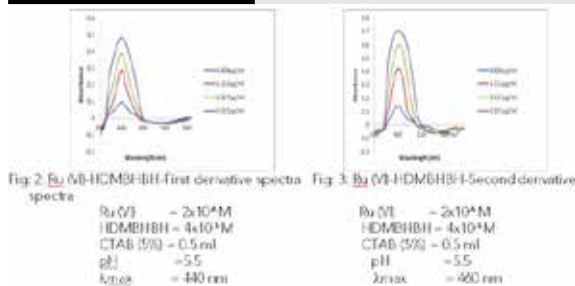
droxy 3,5-dimethoxy benzaldehyde 4-hydroxy benzoylhydrazone (HDMBHBH) was used for the spectrophotometric determination of the Ruthenium (VI). The calibration graph follows the straight-line equation $Y = a + bX$; where c is the concentration of the solution, Y is measured absorbance or peak height and a and b are constants. By substituting the Ru (VI)-HDMBHBH complex experimental data in the Beer's law equation, the calibration equations are calculated as λ_{max} 420 nm = $0.29776X + 0.00141$ for zero order data and λ_{max} 440 nm = $0.24072X + 1.04112 \times 10^{-4}$ for first derivative data and λ_{max} 460 nm = $0.3455X + 0.005$ for second order derivative data which gives the straight lines.



Structure of HDMBHBH Fig: 1: Absorbance Vs Amount of Ru (VI)



$\text{Ru (VI)} = 2 \times 10^{-6} \text{ M}$ HDMBHBH = $4 \times 10^{-3} \text{ M}$
CTAB (5%) = 0.5 ml pH = 5.5
 $\lambda_{max} = 420 \text{ nm}$

**Interference:**

In order to assess the analytical potential of the proposed methods, the effects of some diverse ions which often ac-

company Ru (VI) was examined by carrying out the determination of 1.011 $\mu\text{g/ml}$ of Ru (VI) in the presence of foreign ions for HDM6HBH. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of $\pm 2\%$ in the absorbance or amplitude. The data obtained in the derivative method is also incorporated. The interference of associated metal ions such as Copper (II) and Iron (III) are decreased by adding masking agents Thiourea and Fluoride.

Applications:

The method proposed in the present studies was applied for the determination of Ruthenium (VI) in environmental water and alloy samples.

Table: Estimation of Ru (VI) in Alloy & Water samples

Name of the Alloy Sample	Added	Amount of Ru (VI) mg/ml					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Zn-Mg alloy sample (Zn 50 mg + Mg 50 mg)	5.0	4.992	0.16	4.995	0.10	4.997	0.06
Zn-Mg alloy sample (Zn 50 mg + Mg 50 mg)	5.0	4.994	0.12	4.996	0.08	4.998	0.04
Zn-Mg alloy sample (Zn 20 mg + Mg 20 mg)	3.5	3.493	0.20	3.495	0.14	3.497	0.08
Synthetic alloy sample ($\mu\text{g/g}$) Pb (II) (0.8) + Co (II) (20.0) + Os (VIII) (0.8) + Rh (II) (100)	2.2	2.193	0.31	2.195	0.22	2.197	0.13
River water sample-1	0.450	0.447	0.66	0.449	0.22	0.449	0.22
River water sample-2	0.510	0.507	0.58	0.509	0.19	0.509	0.19

Conclusion:

The proposed methods are simple, accurate and have advantages over the reported methods which suffer from interference by large number of ions or require either heating or extraction or are less sensitive. Some factors such as initial cost of instrument, technical know-how, consumable and costly maintenance of technique restrict the wider applicability of these techniques, particularly in laboratories with limited budget in developing countries and for fieldwork are to be taken as the consideration for the determination of Ruthenium (VI) at microgram quantities, a number of hydrazone derivatives and several analytical techniques such as AAS, ICP-AES, ICP, X-Ray fluorescence spectroscopy and UV-Visible spectrophotometry are employed.

Among them spectrophotometric methods are preferred because they are cheaper and easy to handle. In general

the technique of solvent extraction was widely used in the spectrophotometric determination of metal ions. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction.

Precision and accuracy: The precision and accuracy of the proposed methods are studied by analyzing (10 replicates) of Ruthenium (VI) and the RSD value are found to be less than 1.0 %.

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