SPECTROPHOTOMETRIC DETERMINATION OF Fe (II) AND Fe (III) IN PRESENCE OF MICELLAR MEDIUM USING ORTHO-HYDROXY BENZAMIDE IN PHARMACEUTICAL SAMPLES

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ABSTRACT

Two simple, sensitive, rapid and selective spectrophotometric methods have been developed for the determination of Fe (II) and Fe (III) by using newly synthesized reagent Ortho-Hydroxy Benzamide (SA) in presence of acidic surfactant C-TAB (5%). Fe (II) and Iron Fe (III) forms blue coloured water-soluble complex with SA at pH 5.0 and 5.5 and the complexes shows the maximum absorbance at \( \lambda_{\text{max}} \) 400 and 420 nm for Fe (II) and Fe (III) respectively. At these wavelengths (\( \lambda_{\text{max}} \)), the complex shows maximum absorbance while the reagent blanks shows negligible absorbance. Beer's law was obeyed in the range 0.139-1.396 \( \mu \)g/ml and the optimum concentration range from ringbom plot was 0.279-1.256 \( \mu \)g/ml for Fe (II) and Fe (III) respectively. The molar absorptivity and Sandell's sensitivity for the coloured solution were found to be \( 3.88 \times 10^4 \) L mol\(^{-1}\)cm\(^{-1}\) and 0.0018-\( \mu \)g.cm\(^{-2}\) for Fe (II) and \( 4.81 \times 10^4 \) L mol\(^{-1}\)cm\(^{-1}\) and 0.00116-\( \mu \)g.cm\(^{-2}\) for Fe (III) respectively. The interference effects of various diverse ions have been studied. Fe (II) and Fe (III) forms 1:1 complex with SA stoichiometry with stability constant \( 3.4 \times 10^5 \) for Fe (II) and \( 3.5 \times 10^5 \) for Fe (III). The standard deviation in the determination of 0.558-\( \mu \)g ml\(^{-1}\) of Fe (II) and Fe (III) was found to be 0.0013 and 0.01 respectively. First and second order derivative Spectrophotometric methods was developed at \( \lambda_{\text{max}} \) 420, 440 nm for Fe (II) and at 440, 470 nm for Fe (III) which is more sensitive than the zero order method. The developed method has been employed for the...
determination of Fe (II) and Fe (III) in Synthetic Alloy samples. The results are in good agreement with the certified values.

Keywords: Fe (II) & (III), Spectrophotometry, Synthetic Alloy samples, Micellar medium, CTAB (5%), SA.

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].

Iron occurs in solution in oxidation states +2 and +3. Since ferrous and ferric ions poses chromophoric property, many methods are developed for the photometric determination of metal ion involving the use of reagents without chromophoric property. Most of the Spectrophotometric determination of Iron was based on complexes of Fe (II) [5-8] and comparatively very few for Fe (III) [9]. Bellal and Chabban [10] have determined Fe (II) and Fe (III) colorimetrically in presence of each other.

Salicylamide is the common name for the substance O-hydroxybenzamide, or amide of Salicyl. Salicylamide is a non-prescription drug with Analgesic and Antipyretic properties. Its medicinal uses are similar to those of Aspirin. [11] Salicylamide is used in combination with both Apirin and Caffeine in the over-the-counter pain remedy "Pain Aid".

MATERIALS AND METHODS
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 absorption spectra of reagent (SA) with Fe (II) and Fe (III) complexes under the optimum conditions are shown in Figure 3, 4 & 5, 6.

The calibration graph follows the straight-line equation $Y = a + c + b$; where $c$ is the concentration of the solution, $Y$ is measured absorbance or peak height and $a$ and $b$ are constants. By substituting the Fe (II)-SA and Fe (III)-SA complexes experimental data in the above equation, the calibration equations were calculated as $\lambda_{\text{max}} 400 \text{ nm} = 0.55045X - 0.00273$; $A_{420} \text{ nm} = 0.85618X - 0.00578$ for zero order data and $\lambda_{\text{max}} 420 \text{ nm} = 0.40077X - 0.00231$, $A_{440} \text{ nm} = 0.61442X - 0.00564$ For first derivative data, $\lambda_{\text{max}} 440 \text{ nm} = 0.68463X + 0.00186$, $A_{470} \text{ nm} = 1.1239X - 0.00361$ for second order derivative data which gives the straight lines.

Effect of diverse ions

In order to assess the analytical potential of the proposed methods, the effects of some diverse ions which often accompany Fe (II) and Fe (III) were examined by carrying out the determination of 0.698 µg/ml of Fe (II) and Fe (IIII) in the presence of foreign ions. An ion was considered to interfere in the determination if the absorbance observed differed by more than ± 2% from that for Fe (II) and Fe (III) alone. The results obtained indicate that many metal ions and anions do not interfere in the determination of Fe (II) and Fe (III). However, Cu (II) and Ni (II) interfere seriously as they readily form coloured species with SA. The tolerance limit of Cu (II) and Ni (II) were enhanced by using masking agents of fluoride, phosphate.
Fig. 1&2: Absorbance Vs Amount of Fe (II) & Fe (III)

SA = $5 \times 10^{-3}$
Fe (II) = $2.5 \times 10^{-6}$
pH = 5.0
$\lambda_{\text{max}}$ = 400 nm
CTAB (5%) = 0.5 ml

SA = $5 \times 10^{-3}$ M
[Fe (III)] = $2.5 \times 10^{-6}$
pH = 5.5
$\lambda_{\text{max}}$ = 420 nm
CTAB (5%) = 0.5 ml

Structure of SA

SA = $5 \times 10^{-3}$
Fe (II) = $2.5 \times 10^{-6}$
pH = 5.0
$\lambda_{\text{max}}$ = 400 nm
CTAB (5%) = 0.5 ml

SA = $5 \times 10^{-3}$ M
[Fe (III)] = $2.5 \times 10^{-6}$
pH = 5.5
$\lambda_{\text{max}}$ = 420 nm
CTAB (5%) = 0.5 ml

Fig. 3&4: First derivative spectra

SA = $5 \times 10^{-3}$
Fe (II) = $2.5 \times 10^{-6}$
pH = 5.0
CTAB (5%) = 0.5 ml
$\lambda_{\text{max}}$ = 420 nm

SA = $5 \times 10^{-3}$ M
[Fe (III)] = $2.5 \times 10^{-6}$
pH = 5.0
CTAB (5%) = 0.5 ml
$\lambda_{\text{max}}$ = 440 nm

Fig. 5&6: Second derivative spectra

SA = $5 \times 10^{-3}$
Fe (II) = $2.5 \times 10^{-6}$
pH = 5.0
CTAB (5%) = 0.5 ml
$\lambda_{\text{max}}$ = 440 nm

SA = $5 \times 10^{-3}$ M
[Fe (III)] = $2.5 \times 10^{-6}$
pH = 5.0
CTAB (5%) = 0.5 ml
$\lambda_{\text{max}}$ = 470 nm
Applications: Zero order method: The developed Spectrophotometric methods proposed in the present studies were applied for the determination of Fe (II) and Fe (III) in Pharmaceutical and Synthetic Alloy samples. The results are in good agreement with the certified values.

Table: I. Estimation of Fe (II) and Fe (III) in Pharmaceutical samples

| Pharmaceutical samples | Certified value | Amount found* |          |          |          |          |          |          |          |          |          |          |          |          |          |
|-------------------------|----------------|---------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|                         |                | Fe (II)-SA    | Fe (III)-SA |          |          |          |          |          |          |          |          |          |          |          |          |
|                         |                | Zero order    | Error (%) | D1       | Error (%) | D2       | Error (%) | Zero order | Error (%) | D1       | Error (%) | D2       | Error (%) |          |          |
| Fefonal                 | 2.0            | 1.993         | 0.35      | 1.995    | 0.25      | 1.998    | 0.10      | 1.995     | 0.25      | 1.998    | 0.10      | 1.998    | 0.10      |          |          |
| Orofer                  | 2.0            | 1.99          | 0.5       | 1.993    | 0.35      | 1.995    | 0.25      | 1.989     | 0.55      | 1.993    | 0.35      | 1.995    | 0.25      |          |          |

* Average of five determinations

Table: II. Estimation of Fe (II) and Fe (III) in Alloy samples

| Alloy samples            | Certified value | Amount found* |          |          |          |          |          |          |          |          |          |          |          |          |          |
|--------------------------|-----------------|---------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|                          |                 | Fe (II)-SA    | Fe (III)-SA |          |          |          |          |          |          |          |          |          |          |          |          |
|                          |                 | Zero order    | Error (%) | D1       | Error (%) | D2       | Error (%) | Zero order | Error (%) | D1       | Error (%) | D2       | Error (%) |          |          |
| (a). BAS-85a             | 1.15            | 1.142         | 0.70      | 1.145    | 0.43      | 1.148    | 0.17      | 1.146     | 0.34      | 1.148    | 0.17      | 1.148    | 0.17      |          |          |
| (b). Ferrovanadium       | 47.217          | 47.213        | 0.40      | 47.215   | 0.20      | 47.215   | 0.20      | 47.213    | 0.40      | 47.215   | 0.20      | 47.215   | 0.20      | 0.20      |          |
| (c). Lincolnshire Iron ore (BCS-301/1) | 23.8           | 23.62         | 0.76      | 23.65    | 0.63      | 23.77    | 0.12      | 23.74     | 0.25      | 23.78    | 0.08      | 23.78    | 0.08      |          |          |

* Average of five determinations
Precision and accuracy: The precision and accuracy of the proposed methods are studied by analyzing (10 replicates) of Fe (II) and Fe (III) and the RSD values are found to be less than 0.3%.

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 Fe (II) and Fe (III) 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.

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