Spectrophotometric determination of iron(III) in ore, pharmaceutical formulations, plant material and foodstuff using piroxicam

M B Melwanki, J Seetharamappa & S P Masti
Department of Chemistry, Karnataka University, Dharwad 580 003, India

Received 21 September 2001; revised 30 September 2002

Piroxicam (PR) has been proposed as a sensitive and selective reagent for the spectrophotometric determination of Fe(III) in ore, pharmaceutical formulations, plant material and foodstuff. The method is based on the formation of a chloroform-soluble red coloured 1:1 complex by the reaction of Fe(III) with PR in Walpole buffer. Beer’s law is valid over the concentration range of 0.4-6.4 ppm. The coloured complex exhibits an absorption maximum at 510 nm with molar absorptivity of 1.82×10^4 1 mol^-1 cm^-1 and Sandell’s sensitivity of 17.32 ng cm^-2. The absorbances are found to increase linearly with increase in concentration of iron, which are corroborated by the calculated correlation coefficient value (0.9992). The effects of foreign ions in the determination of Fe(III) have been studied. Statistical comparison of the results with those of direct AAS method shows good agreement and indicates no significant difference in precision.

Iron(III) serves as a key component of the enzyme system and proteins with vital functions at optimum levels. Excess intake of iron causes siderosis, while its deficiency causes anaemia. Iron compounds find applications in industry as catalysts, in agriculture as pesticides and in textile industry as dyes and pigments. Consequently, there is a need for the development of a rapid, sensitive and low-cost analytical methods for the determination of iron. Neutron activation analysis and atomic absorption spectrophotometric methods used for the determination of iron are quite costly and cumbersome for routine field measurements. Hence, we attempted to develop a simple and sensitive spectrophotometric method for the determination of iron in ore, pharmaceutical formulations, plant material and foodstuff.

Investigations have shown that Fe(III) reacts with piroxicam(PR), 4-hydroxy-2-methyl-N-2-pyridinyl-2-H-1,2-benzothiazine-3-carboxamide 1,1-dioxide, to form a chloroform-soluble red colored complex in Walpole buffer. The chromogen formed in the proposed method is more stable when compared to those of the reported methods (30-60 min) and also has higher sensitivity (ε =1.82×10^4 1 mol^-1 cm^-1) than those of the earlier methods (ε=3.5-9.3×10^3 1 mol^-1 cm^-1). Moreover, the proposed method is free from interference by a large number of metal ions unlike the reported methods.

Experimental

A Hitachi (Model U-2001) UV-visible spectrophotometer with 1 cm matched quartz cells was used for the absorbance measurements and PH measurements were made on a Schott Gerate PH meter (CG 804). A double beam atomic absorption spectrophotometer (GBC 902) was used for the study. Elemental analysis of the complex was performed on a Thermoquest CHN analyser (Model EA 1110 CHN).

All the chemicals used were of analytical or pharmaceutical grade and quartz-processed high-purity water was used throughout. A stock solution of Fe(III) was prepared by dissolving ferric ammonium sulphate (AR) in a small quantity of sulphuric acid and diluting with distilled water. The stock solution was standardised volumetrically. It was diluted as and when required. A 0.5% solution of PR was prepared in methanol and stored in an amber-colored bottle in a refrigerator. Walpole buffers of different pH were prepared from 1 M sodium acetate and 1 M hydrochloric acid. Solutions of diverse ions of suitable concentrations were prepared using AR grade reagents.

General procedure

To a known volume of Fe(III) solution taken in a series of separating funnels, were added Walpole buffer (1.5 ml, PH 5.0) and of 0.5% PR (2 ml). Ten milliliters of chloroform were added and shaken well. Two phases were allowed to separate and the chloroform layer was passed through anhydrous sodium sulphate. The absorbance of the red colored complex was measured at 510 nm against the reagent blank. The amount of Fe(III) in the sample was deduced from the calibration curve.

Analysis of iron(III) in haematite ore

About 0.5 g of haematite ore was weighed accurately and treated with concentrated hydrochloric
acid (10 ml), water (10 ml) and nitric acid (2 ml). The solution was digested at a low flame on a sand bath to almost dryness. The hydrochloric and nitric acids treatment was repeated till the ore was dissolved completely. The insoluble silica was filtered off using Whatman filter paper No. 41 and the filtrate was diluted to 100 ml in a calibrated flask. An aliquot of the filtrate was taken, pH of it was adjusted to 5.0 and the amount of iron(III) was determined using the procedure described for pure Fe(III).

Analysis of iron(III) in pharmaceutical samples
The contents of the tablets or capsules were ignited in a muffle furnace at 400°C for 1.5 h. The ash was dissolved in concentrated hydrochloric acid (5 ml), filtered and diluted to 100 ml with distilled water. Suitable amounts of aliquot of the solution were taken, pH of the solutions were adjusted to 5.0 and the amounts of Fe(III) were determined by following the procedure described earlier.

Analysis of iron(III) in pine needles
A known amount (about 1 g) of pine needles was weighed accurately in to a crucible and heated at low temperature to char the sample, then at higher temperature to drive off most of the carbon, and finally at 800-900°C to ash the sample completely. The contents were cooled to room temperature and moistened with 2-3 drops of concentrated nitric acid, evaporated to dryness, and again ignited at 800-900°C for 1 h. After cooling, the ash was dissolved in 5 ml of concentrated hydrochloric and transferred in to a 100 ml calibrated flask. It was diluted up to the mark with distilled water and the amount of iron(III) was determined using the procedure given earlier.

Analysis of iron(III) in rice
The rice sample was dried in oven at 90°C for 20 h. A known amount (about 5 g) of the sample was weighed accurately, digested with nitric acid and perchloric acid and heated gently on a hot plate to dryness. The ash was treated with concentrated hydrochloric acid (5 ml) and evaporated to dryness. The residue was extracted with concentrated hydrochloric acid (2 ml), filtered and the volume was made to 25 ml with distilled water. An aliquot of the solution was taken, pH of it was brought to 5 and the amount of iron(III) was determined using the procedure given above.

Results and discussion
It was observed that Fe(III) reacts with PR in Walpole buffer to form a chloroform-soluble red colored complex which exhibits an absorption maximum at 510 nm. The reagent blank does not absorb at 510 nm. The optimum reaction conditions for quantitative determination of the complex were achieved via a number of preliminary studies. Complex formation was not observed in hydrochloric, sulphuric and phosphoric acids media. The effect of Walpole buffer on the formation of the complex was studied over the pH range 1.0-5.2. It was found that the absorbances remained constant over the pH range of 4.0-5.2. However, 1.5 ml of buffer of pH 5 was used for the study. A volume of 1.5 ml of PR was found to be sufficient for maximum colour intensity and constant absorbances of the complex. It was also observed that the excess of the reagent had no effect on \( \lambda_{\text{max}} \) or sensitivity or on stability of the complex. Hence, a 2.0 ml of PR was used to ensure complete reaction.

Of the several organic solvents tried for quantitative extraction of the complex, chloroform was found to be the most suitable solvent. It was observed that there was no appreciable change in sensitivity, stability or \( \lambda_{\text{max}} \) of the coloured complex even if the order of addition of reagents was changed. The absorbances of the complex were found to be stable for more than 20 h.

The red coloured complex obeyed Beer's law in the range of 0.4-6.4 ppm of iron(III) with molar absorptivity value of 1.82 x 10^4 1 mol^-1 cm^-1. Sandell's sensitivity value as calculated from Beer's law data was found to be 17.32 ng cm^-2. Regression analysis of Beer's law plot at 510 nm revealed a good correlation (r=0.9992). Graph of the absorbance versus the concentration showed low intercept value (0.0198) and slope (0.1124) and is described by a regression equation, \( Y = a + bX \) (where \( Y \) is the absorbance of a 1 cm layer, \( b \) is the slope, \( a \) is the intercept and \( X \) is the concentration of iron(III) in ppm), obtained by the least-squares method. The low values of relative standard deviation (0.91) and the range of error at 95% confidence level (0.71) for the analyses of five replicates of 4 ppm of iron(III) indicated good precision and accuracy of the proposed method.

The stoichiometry of the complex was studied spectrophotometrically using Job's method of continuous variation and molar ratio methods. The results indicate that the mole ratio between iron(III) to
PR is 1:1. The analytical data of the complex obtained in solid form by evaporating the chloroform layer also confirms the composition to be 1:1.

**Effect of diverse ions**

To assess the analytical potential of the proposed method, the effects of some diverse ions which are usually associated with iron were determined by measuring the absorbance of a solution containing 4 ppm of Fe(III) and various amounts of diverse ions. The following are the tolerance limits (ppm) for the ions: Cr(VI), 6000; Mn(II), 500; Pb(II), 1500; Zn(II), 500; Hg(II), 600; Na(I), 3000; K(I), 3500; Ca(II), 3000; Mg(II), 2700; Cd(II), 1000; Zr(IV), 30; Mo (VI), 20; Ni(II), 22; Cu(II), 10; Cu(II)*, 200 in presence of 1000 ppm of thiourea; Co(II), 25; chloride, 8000; acetate, 5000; tartarate, 4500; bromide, 1200; phosphate, 3000; fluoride, 500; thioanate, 4000; thiourea, 1500; iodide, 750. From these results it is clear that the proposed method could be effectively applied for the determination of iron(III) when many foreign ions were present even in large excess.

**Applications**

The applicability of the proposed method was checked by analyzing the amounts of iron(III) in ore, pharmaceutical formulations, plant material, and foodstuff. The results presented in Table 1 are in good agreement with those obtained by the direct Atomic Absorption Spectrophotometric (AAS) method.

**Statistical analysis of the results in comparison with the AAS method**

The results of the analysis of ore, pharmaceutical formulations, plant material, and foodstuff were compared statistically by Students t-test and by the variance ratio F-test with those obtained by the direct AAS method. The Students t-values at 95% confidence level did not exceed the theoretical value indicating that there was no significant difference between the proposed and the AAS methods. It was also noticed that the variance ratio F-values calculated for p=0.05 did not exceed the theoretical value indicating that there was no significant difference between the precision of the proposed method and the direct AAS method. The results are shown in Table 1.

Thus the proposed procedure offers the advantages like reliability and reproducibility in addition to its simplicity. The proposed method could be thus used as an alternative method for the investigation of micro amounts of iron in ore, pharmaceutical formulations, plant material and foodstuff as the associated substances in these materials do not interfere in the determination of iron.

**Acknowledgements**

The authors are thankful to Cipla Ltd. for the gift sample of pure piroxicam. Thanks are also due to the Chairman, Department of Chemistry, Karnataka University, Dharwad for providing necessary facilities.

**References**


<table>
<thead>
<tr>
<th>Sample taken</th>
<th>Iron (III), ppm</th>
<th>Comparison with AAS method</th>
<th>RSD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cert²</td>
<td>AASb method</td>
<td>present methodc</td>
<td>Comparison with AAS method at 95% confidence limit</td>
</tr>
<tr>
<td>Tablets</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zifal – 12</td>
<td>4.46</td>
<td>4.36</td>
<td>0.79</td>
</tr>
<tr>
<td>Irox – 12</td>
<td>5.07</td>
<td>5.20</td>
<td>0.88</td>
</tr>
<tr>
<td>Farnium</td>
<td>3.55</td>
<td>3.49</td>
<td>0.83</td>
</tr>
<tr>
<td>Aurin</td>
<td>2.24</td>
<td>2.29</td>
<td>0.95</td>
</tr>
<tr>
<td>Haematite</td>
<td>88.75 %</td>
<td>87.5 %</td>
<td>0.69</td>
</tr>
<tr>
<td>Rice I</td>
<td>43.41</td>
<td>42.85</td>
<td>0.85</td>
</tr>
<tr>
<td>Rice II</td>
<td>44.91</td>
<td>45.22</td>
<td>0.94</td>
</tr>
<tr>
<td>Pine needles I</td>
<td>155.6</td>
<td>154.1</td>
<td>0.77</td>
</tr>
<tr>
<td>Pine needles II</td>
<td>170.2</td>
<td>172.0</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Average of five determinations

References: