Spectrophotometric determination of iron in water samples using 3-Hydroxy Benzyl Amino Benzoic acid

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doi:10.6088/ijes.2012030131020

ABSTRACT

3-hydroxy benzyl amino benzoic acid has been synthesized by the author in the laboratory which could be used successfully to estimate the amount of iron present in the water samples. This reagent-iron complex gave good absorption spectra with absorption maximum at 480 nm. n-butanol was used as the solvent, a pH of 5.0 was maintained, the reagent concentration was chosen as 6.0 X 10^{-3} M and there was no interference of foreign ions. With these standardized parameters, more than 90% recovery of added iron was found in the samples with the present method. The value obtained with the present reagent was compared with standard reagent to be in good agreement, indicating the usefulness of the reagent for accurate spectrophotometric determination of iron in water samples.

Keywords: 3-hydroxy benzyl amino benzoic acid, Iron, Water samples.

1. Introduction

Iron is an essential nutrient required in trace quantities for all living cells of plants and animals for their normal metabolism. Iron is vital for almost all living organisms due to the fact that it occurs in a wide variety of metabolic processes, including oxygen transport, DNA synthesis, and electron transport (Lieu et al., 2001). However, iron concentrations in body tissue must be carefully regulated, because excessive iron leads to tissue damage as a result of formation of free radicals (Burtis.,1994). Iron deficiency in human adults manifests clinically by fatigue, palpitation on exertion and sometimes by a sore tongue, angular stomatitis and dysphagia. Iron overloads have been associated with haemochromatosis, a genetic disorder of iron metabolism, characterized by a brown discoloration of the skin and other organs. Determination of iron, both at microgram and milligram levels, may therefore be of considerable importance. Iron occurs in solution both in +2 and +3 states. Iron (III) is one of the most easily extracted species. Hence, its masking or pre-extraction is an important step in separating it from other metal ions. A change in its oxidation state from +2 to +3 and vice-versa occurs easily, but the distribution behavior of the two ions in solutions is however different. Iron is included in the quality control of industrial and commercial products such as petroleum, alloys, foods, beverages etc (Toral., 1997). Thus, the determination of trace amounts of these analytes is becoming increasingly important, especially with respect to environmental pollution. (Yamini et al., 2001) reported a simple and reliable method for the rapid extraction, separation, preconcentration, and determination of iron as its bathophenanthroline complex by the use of octadecylsilica membrane disks and spectrophotometry. Picolinaldehyde 4-phenyl-3-thiosemicarbazone as a spectrophotometric reagent for the selective determination of small amounts of cobalt in the presence of iron was developed by (Ariza et al., 1976). Various chelating agents, such as 1-(2-pyridylazo)-2-naphthol (PAN) (Taher, M.A., 2000), Dimethyl (E)2-(2-Methoxyphenoxy)-2-butenedioate
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(Khayatian, G et al., 2010), 2', 3', 4', 5, 7-Pentahydroxyflavone (Ahmed, M. J et al., 2009), 2-hydroxy-3-methoxybenzaldehyde-isonicotinoylhydrazone (Anusuya Devi et al., 2011), 3-((indolin-3-yl)(phenyl)methyl)indoline (Ghaedi, M et al., 2010), N,N'-Diaetyl-4-bromo-2,6-di(aminomethyl)anisole (Ghaedi, M et al., 2009), 1-phenyl-3-methyl-4-benzoylpyrazolone (PMBP) [(Xiaa, L et al., 2003), Dimethyl(E)-2-(methoxyphenoxy)-2-butenedioate (Khayatian, G et al., 2010)] 2', 3', 4', 5, 7-pentahydroxyflavone (Asan, A et al., InPress) and many authors (Chen, H et al., 2012, Nazzal, Y et al., 2012), have been reported in literature for the determination of iron in various samples.

2. Materials and method

2.1 Experimental

All starting materials required for the preparation of the reagent were of analytical reagent grade. All the solvents used were double distilled before use. These included chloroform, methyl isobutyl ketone, carbon tetrachloride, benzene, n-butyl alcohol, amyl alcohol, dimethyl formamide and ethyl alcohol. Reagents, standard solutions of metal ions and various other solutions required in the present investigations have been prepared following the standard procedures. A digital pH meter, Model LI-120 (ELICO), with combined glass electrode assembly was employed for reckoning pH studies. The sensitivity of the instrument was ± 0.001 pH units. A Systronics UV-VIS double beam Spectrophotometer model 118 with 1.00 cm optical path quartz cells was employed to carry out the spectrophotometric studies. The chelating agent used in the present investigation was prepared using the method reported [(Kumar, A.P et al., 2007; Afkhami, A et al., 2009; Reddy, K.H et al., 2003). 1.0 g of 3-hydroxy benzaldehyde was dissolved in 25 ml of double distilled water and mixed in a flask with 1.0 g of 4-amino benzoic acid and refluxed for 3 hours. A pale yellow colored crystal product was formed. After filtering the product, it was dried at room temperature. Finally the product was recrystallized by using ethanol. The resulting product has melting point of 165°C and the yield was 80-90%. The above reaction is shown in Figure 1.

![Figure 1: Schematic diagram of 3-hydroxy benzyl aminobenzoic acid](image)

3. Results and discussion

3-hydroxy benzyl amino benzoic acid yields a yellow colored complex with iron(III) solution in sodium acetate-acetic acid buffer of pH 5.0. This complex has maximum absorption at 480 nm and is stable for five hours. The conditions for effective extraction were established after studying the effects of various factors such as pH, choice of the solvent, reagent concentration and diverse ions, in order to develop a sensitive spectrophotometric method for determination of iron(III) in various water and industrial waste samples.
3.1 Absorption spectrum of the 3-hydroxy benzyl amino benzoic acid – iron complex

An aliquot of 1.0 ml of iron (III) solution was transformed into a 25 ml separating funnel. To it, 1.0 ml of 3-hydroxy benzyl amino benzoic acid in a aqueous dimethyl formamide solution and 3.0 ml of pH 5.0 buffer solution were added. Then the yellow colored complex was transferred into a 25 ml standard flask and made up to the mark. The reagent blank was prepared by using the same solutions without iron (III) and extracted similarly. The absorption spectrum of the complex is recorded against the reagent as a blank. The absorption spectrum of the reagent complex is shown in Figure 2. The spectrum reveals that the Fe(III)-3-hydroxy benzyl amino benzoic acid complex gives maximum absorbance at 480 nm. Hence, further absorbance measurements of the complex were made at 480 nm.

![Absorption Spectrum of the Reagent Complex](image)

**Figure 2: Absorption Spectrum of the Reagent Complex**

3.2 Choice of solvent

In this method various organic solvents such as MIBK, n-butanol, benzene, chloroform, carbontetrachloride, ethyl acetate etc., were used for the extraction of reagent-metal complex. Maximum absorbance was obtained with n-butanol. Hence, n-butanol solvent was chosen in further investigations.

3.3 Effect of pH

The buffer solutions used in the extraction of Fe(III)-reagent solution were sodium formate-formic acid (pH 2.6-3.4), sodium acetate-acetic acid (pH 3.4-6.5) and ammonium chloride-ammonium hydroxide (pH 7.0-11.0). In each case, a mixture containing 50.0 µg of iron (III), 3.0 ml of the suitable buffer and 1.0 ml of reagent solution were taken and the volume was adjusted to 10.0 ml with double distilled water. The experiment was repeated with buffers of different pH values from 3.0-8.0 The plot between pH and its absorbance is shown in Figure 3. It is observed that the extraction of the metal ion increases as the pH increases from 3.0, and remains constant in the pH range of 4.5-6.5. However, it decreases from 6.5 onwards. Hence, pH 5.0 is fixed for further studies, considering it as the optimum pH value.
Variation of absorbance with concentration of interfered negatively

3.4 Effect of reagent concentration

The effect or reagent concentration has been studied by keeping 1.0 ml of iron (III) solution and 3.0 ml of pH 5.0 buffer constant. The concentration of 3-hydroxy benzyl amino benzoic acid was varied between $1.0 \times 10^{-3}$ M and $11.0 \times 10^{-3}$ M to obtain maximum color formation. The total volume of aqueous phases was brought to 10.0 ml with double distilled water. The aqueous phases were shaken with 10.0 ml of n-butanol in each case; the organic phases collected in 25 ml standard flasks and made upto 25 ml with n-butanol. The absorbance of these phases was measured at 480 nm, against their corresponding reagent blanks. The spectrum is shown in Figure 4. The experiment revealed that a $6.0 \times 10^{-3}$ M of reagent to that of metal ion is sufficient for maximum color development of the complex. Hence, a six-fold molar excess of the reagent is maintained for all further studies.

Figure 4: Variation of Absorbance with Concentration of 3-hydroxy benzyl amino benzoic acid reagent with iron

3.5 Effect of foreign ions

In order to assess possible analytical applications of the method, the effect of diverse ions on the extraction and spectrophotometric determination of iron(III) were studied. Tolerance limits were determined for a maximum error of 5%. NaCl and NaNO$_2$ interfered negatively with the spectrophotometric measurements when they were present at 1000 and 750 times of
the iron concentration. The result indicates that metallic and anionic species had no adverse effect on the analytical signal(s) of Fe.

3.6 Stability of the color reaction

The absorbance values of Fe(III)-3-hydroxy benzyl amino benzoic acid complex were noted at different intervals of time at 480 nm. It was observed that the absorbance remained constant up to five hours, thereby indicating that the color of the complex is stable for at least five hours.

3.7 Sensitivity and molar absorptivity of Fe(III)-3-hydroxybenzyl amino benzoic acid complex

The molar absorptivity of the complex was calculated and reported as $2.1 \times 10^4$ lit mol$^{-1}$ cm$^{-1}$ and the Sandell’s sensitivity of the complex was found to be $2.243 \times 10^{-3}$ µg cm$^{-2}$.

4. Applications of the developed method

The procedure developed for the determination of iron (III) was successfully used to determine the content of iron in various water samples.

Analysis of various water samples

Water samples were collected from industrial areas in and around Tirupati. Pre-treatment of water samples was done, as per standard procedure described in the literature and analysed for Fe (III) by the present analytical procedure. The results are shown in Table 1 which shows a good recovery of the iron added using the present reagent. The estimation of iron made using the present method is compared with another method using a standard reagent Ethylene diamine and the results are in good agreement as shown in Table 2.

Table 1: Determination of iron in various water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iron added (µg ml$^{-1}$)</th>
<th>Proposed method</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Found$^a$ (µg ml$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>Polluted water$^b$</td>
<td>-</td>
<td>0.23 ± 0.02</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0.30 ± 0.04</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0.42 ± 0.03</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0.49 ± 0.01</td>
<td>-</td>
</tr>
<tr>
<td>Natural water$^c$</td>
<td>1.0</td>
<td>1.50 ± 0.02</td>
<td>95.20</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>2.04 ± 0.06</td>
<td>92.66</td>
</tr>
<tr>
<td>Bore well water$^d$</td>
<td>-</td>
<td>1.0 ± 0.02</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>1.06 ± 0.04</td>
<td>-</td>
</tr>
<tr>
<td>Drinking water$^e$</td>
<td></td>
<td>0.50 ± 0.04</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.46 ± 0.02</td>
<td>96.36</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>2.02 ± 0.04</td>
<td>95.22</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>2.34 ± 0.02</td>
<td>92.66</td>
</tr>
</tbody>
</table>

a) Mean ± standard deviation (n=5), b) Collected near Gajulamanyam industrial area, A.P., India, c) Collected from Swarnamukhi river, Srikalahasti, A.P, India. d) Collected from in and around Tirupati, e) Collected from Telugu Ganga water supply, Tirupati.
Table 2: Determination of iron in various water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard method(^a) (µg ml(^{-1}))</th>
<th>Present method (µg ml(^{-1}))</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polluted water(^b)</td>
<td>0.38</td>
<td>0.30 ± 0.02</td>
<td>80.00</td>
</tr>
<tr>
<td>Natural water(^c)</td>
<td>0.60</td>
<td>0.56 ± 0.04</td>
<td>93.54</td>
</tr>
<tr>
<td>Bore well water(^d)</td>
<td>1.0</td>
<td>1.0 ± 0.01</td>
<td>100.00</td>
</tr>
<tr>
<td>Drinking water(^e)</td>
<td>0.44</td>
<td>0.42 ± 0.02</td>
<td>96.30</td>
</tr>
</tbody>
</table>

\(^a\) Using Ethylenediamine procured from local market  
\(^b\) Collected near Gajulamanyam industrial area, A.P., India  
\(^c\) Collected from Swarnamukhi river, Srikalahasti, A.P, India  
\(^d\) Collected from in and around Tirupati  
\(^e\) Collected from Telugu Ganga water supply, Tirupati.

5. Conclusion

From the above discussions, it is evident that 3-hydroxy benzyl amino benzoic acid is a good sensitive fragment for the extractive spectrophotometric determination of iron(III) in water samples. Hence, the use of 3-hydroxy benzyl amino benzoic acid as an extractant in the separation of iron(III) from several other associated metal ions is commendable. The proposed method is highly sensitive when compared to the reported methods for the spectrophotometric determination of iron(III) in various samples. It offers advantages like reliability and reproducibility, in addition to its simplicity, instant color development and less interference.

Acknowledgement

The author would like to thank Prof.K.Janardhanam and P.Nagaraju, Department of Environmental Sciences, Sri Venkateswara University, Tirupati, in the laboratory for providing assistance to fulfill the experiment in a proper manner.

5. References


5. Ariza, J.L., Pavon, J.M., Pino, F., (1976), Picolinaldehyde 4-phenyl-3-thiosemicarbazone as a spectrophotometric reagent for the selective determination of small amounts of cobalt in the presence of iron, Talanta, 23(6), pp 460-462.


