Chapter 3

EXTRACTION SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF IRON WITH TETRAPHENYLARSONIUM CHLORIDE

Introduction:

Large number of organic reagents give sensitive colour reactions with iron. The most extensively used one such reagent which forms red colour with ferric iron is thiocyanate.\(^1,2,3\) The coloured complex was also extracted by ether,\(^4\) isoamyl alcohol,\(^5\) ethylacetate,\(^6,7\) and isobutanol\(^8\) and the amount of iron was determined by measuring the absorbance of these extracts at specified wavelength. Determination of iron using 1,10-phenanthroline\(^9\) is the most widely used method which is based on the formation of a red complex between ferrous ion and 1,10-phenanthroline. Moreover procedures for the determination of iron based on the formation of iron complexes with sulphosalicylic acid,\(^10\) salicylic acid,\(^11\) salicylaldoxime,\(^12\) 2,2'-bipyridine,\(^13\) bathophenanthroline,\(^14\) 2,2'-bipyridyl,\(^15\) thioglycolic acid,\(^16\) nitroso-\(\text{H}\)-salt,\(^17\) ferron,\(^18\) \(\alpha\)-picolinic acid with cyanide,\(^19\) 5-sulphoanthranilic acid,\(^20\) kojic acid,\(^21\) meconic acid,\(^22\) etc. have been suggested. New spectrophotometric methods based on complex formation with sodium salt of schiff base,\(^23\) calcichrome\(^24\) were also described.

Amongst inorganic colour forming reagents with iron, concentrated hydrochloric acid, concentrated hydrobromic acid and perchloric acid have been investigated. Futtner\(^25\) reported hydrochloric acid as one of the simplest colorimetric reagent.
Subsequently, colorimetric determination of iron in hydrochloric acid was done. Recently, the possibility of extraction of acid complex of iron in hydrochloric acid as ion-association complex with tetraphenylarsonium chloride into dichloroethane has been reported. We have also found that the acid complex of iron in hydrochloric acid is not extracted at all into 1,2-dichloroethane in absence of tetraphenylarsonium chloride. However, on addition of tetraphenylarsonium chloride to the aqueous solution of iron, \( \text{Fe}^2+ \) in hydrochloric acid, iron is quantitatively extracted into 1,2-dichloroethane. This has led us to investigate the possibility of extractive spectrophotometric determination of iron in micro amounts based on the extraction of its ion-association complex with tetraphenylarsonium chloride from hydrochloric acid medium into 1,2-dichloroethane.

**Experimental:**

**Apparatus:**

Absorption spectrum in the particular wavelength region was taken and absorbance measurements were made with a Beckman DU-2 spectrophotometer. At times, absorbance at specific wavelength was also measured in the Hilger Uvispek Photoelectric spectrophotometer.
Reagents:

Most of the chemicals used were of analytical grade.

Solvent:

Laboratory grade 1,2-dichloroethane procured from B.D.H. was redistilled for use as solvent.

Standard iron solution:

A stock solution was prepared by dissolving 0.1080 g of ferric ammonium sulphate (A.R., B.D.H.) in 2N hydrochloric acid (prepared from concentrated analar acid) and was made up to 100 ml with it for using as a stock solution. Solution of lower concentrations were prepared by dilution, from the stock solution, with 2N hydrochloric acid.

Reagent solution:

A 0.001N solution of tetraphenylarsonium chloride (Fluka A.G., Buchs SG) in 1,2-dichloroethane was employed as the reagent.

Other chemicals:

Other metal compounds used for studying interferences were cadmium sulphate, copper sulphate, mercuric chloride, zinc sulphate, manganous sulphate, chromic sulphate, antimony chloride, stannic chloride, chloroauric acid, ammonium molybdate, sodium tungstate, potassium chromate, potassium
permanganate, ammonium thiocyanate, potassium tartrate, ammonium fluoride, oxalic acid, sodium vanadate, and perchloric acid.

Preliminary studies on the extraction and spectrophotometric determination of iron:

Absorption spectra:

The absorption spectra of a solution of tetraphenyl arsonium tetrachloro ferrate complex in 1,2-dichloroethane obtained by extracting an acidic solution of iron containing 20 µg of iron with tetraphenyl arsonium chloride was taken in Beckman DU-2 spectrophotometer in the region 440 to 330 nm against the solvent (Fig. 1). The absorption maximum of the complex was found to be at 363 nm. The reagent blank against solvent showed no absorption in this region. Hence all the absorbance measurements were carried out at 363 nm against solvent as reference using 1 cm quartz cell.

Variation of absorbance with acid concentration:

In order to examine the effect of acidity of the aqueous layer in the extraction of iron, 5 ml of standard solution containing 20 µg of iron(III) was taken in several different separating funnels. Normality of each of the solution was varied from 2N to 5N with respect to hydrochloric acid by adding varying amount of standard acid. To each of these was then added 5 ml of 0.001N tetraphenyl arsonium chloride reagent in 1,2-dichloroethane, and the resulting mixture was shaken for
Fig. 1. Absorption spectra of tetraphenylarsonium tetrachloro ferrate in 1,2-dichloroethane containing 4 μg of iron per c.c. against solvent (A), (B) the spectrum of the reagent blank against solvent.
5 minutes. The absorbance of the extracts were then measured at 363 nm. There was no significant change in the absorbance value of the ion-pair, extracted from aqueous solution of higher acidity beyond 2N. However, at higher acidity, the reagent itself is precipitated as is seen by adding an aqueous solution of tetraphenylarsonium chloride. Extraction was, therefore, carried out from 2N hydrochloric acid to avoid use of large excess of the reagent.

**Effect of tetraphenylarsonium chloride concentration on absorbance:**

The extraction of iron, taking aliquots containing 20 μg of iron was carried out with 5 ml of the reagent solution of varying concentration ranging from 0.001M to 0.01M. The absorbance of the resulting extract of the complex was measured at 363 nm. The absorbance value was maximum and was the same at the lowest concentration as it was at higher concentrations, showing quantitative extraction of iron even with the lowest concentration of the reagent, i.e., 0.001M. As such, 5 ml of 0.001M solution of the reagent was found to be more than enough for the quantitative extraction of iron.

**Variation of absorbance with time:**

An aliquot of the standard solution containing 20 μg of iron was taken to which 5 ml of 0.001M tetraphenylarsonium chloride reagent in 1,2-dichloroethane was added and then shaken for 5 minutes. After extraction, absorbance of the
extract at 363 nm was measured at different time intervals. The variation of absorbance with time is shown in Fig. 2.

**Analytical and separation procedure:**

Aliquots of the standard solution containing 5 to 40 μg of iron were taken in each of the several different separating funnels. The volume in each was made up to 5 ml with 2N hydrochloric acid. To each of these solutions was then added 5 ml of 0.001M tetraphenylarsonium chloride in 1,2-dichloroethane and the resulting mixture was shaken for 3 minutes. The organic layer in each was separated and absorbance measurement of the extract was made at 363 nm. A standard calibration curve, obtained by plotting these absorbance values against iron concentrations is shown in Fig. 3. The ion-pair, tetraphenylarsonium tetrachloro ferrate, in the organic phase conforms to Beer's law over the concentration range of 5 to 40 μg of iron per 5 ml of the extract.

Aliquots of the iron solution for the determination of iron in other samples, were treated in a similar manner and their 1,2-dichloroethane extracts were measured at 363 nm. The amount of iron was then calculated from the standard calibration curve. The results which are the average of five determinations, in each case, are shown in Table 1.

**Studies on the interferences due to other ions in the determination of iron:**

In a separate set of experiments, an aliquot of the standard solution containing 20 μg of iron was taken in each of
FIG. 2. Variation of absorbance with time.
FIG. 3 CALIBRATION CURVE FOR IRON
the several different separating funnels. To each of these solutions of metal ions, viz., copper(II), cadmium(II), manganese(II), chromium(III), tin(IV), zinc(II), antimony(III), mercury and anions molybdate, chromate, oxalate, fluoride, perchlorate, thiocyanate, vanadate, tungstate, permanganate, tartrate and aurrate in amounts equal to and ten times the amount of iron was added. The volume, in each, was made 5 ml, making the solution 2N with respect to hydrochloric acid. To each of these solutions was then added 5 ml of 0.001 N tetraphenylarsonium chloride in 1,2-dichloroethane. The resulting mixture was shaken for 3 minutes and the organic layer was separated. Absorbance measurements of the extracts were then made as above at 365 nm. The results showing the recovery of iron are given in Table 2.

Results and discussion:

The halo complex of iron(III) exists in 2N hydrochloric acid, forms an ion-pair with tetraphenylarsonium chloride and the resultant ion-association compound was found to be extractable into 1,2-dichloroethane. The yellow coloured extract has an absorption maximum at 365 nm and obeys Beer's law over the concentration range 1 to 5 µg per ml. The sensitivity of the method was found to be 0.005 µg of iron per ml per cm. The maximum error involved in the determination of trace quantities of iron in absence of other ions is within 2.5%.
Dependence of absorbance of the tetraphenyl arsonium tetrachloro ferrate complex on various factors, viz., acidity of the aqueous layer, reagent concentration, stability of colour with time and temperature was studied.

Extraction of tetraphenyl arsonium tetrachloroferrate complex is possible from solution which is 2N with respect to hydrochloric acid. Examination of the acid concentration showed that the absorbance of the extract remains constant with increasing acidity from 2N to 5N. However, at higher concentration of hydrochloric acid, a large proportion of the reagent is reformed in the aqueous layer and comes to the organic phase. In other words, the reagent remains as such in the organic phase, thus lowering the availability of tetraphenyl arsonium cation in the aqueous layer. Besides, higher hydrochloric acid concentration facilitate formation of halo complexes by other metals which might result in interference. Acidity of the aqueous layer was, therefore, maintained at 2N to reduce the chloride ion concentration.

The extraction of iron(III) at varying concentration of tetraphenyl arsonium chloride revealed that a 0.001 \text{M} solution of the reagent was found to be most suited for quantitative extraction. 5 ml of 0.001\text{M} tetraphenyl arsonium chloride in 1,2-dichloroethane was thus found to be sufficient for the determination of 5 to 40 \text{ug} of iron.

The absorbance of the complex in 1,2-dichloroethane was measured at elapsed intervals of 5, 10, 30, 60, 90, 120, 180, 240 and 300 minutes after extraction. The absorbance value
was found to be stable up to 10 minutes. Therefore all the
absorbance measurements were made within three hours of its
extraction. The absorbance of the complex is independent of
temperature in the range 20°C to 35°C.

An examination of the effect of the presence of other
metal ions, viz., cadmium(II), copper(II), mercury(II), zinc(II),
manganese(II), chromium(III), antimony(III), tin(IV), showed
that these metals when present in equal amounts with iron did
not interfere (error within 2.5%). However, tin(IV) and
antimony(III) in their ten-fold excess interfered. A similar
study on the effect of the presence of common anions, viz.,
AuCl₄⁻, NO₃⁻, SO₄⁻², CrO₄²⁻, MnO₄⁻, CN⁻, F⁻, CO₃²⁻, V₅O₆⁻², and ClO₄⁻¹ showed that only CrO₄²⁻, CN⁻, and MnO₄⁻¹
interfered seriously when present in equal amounts and in ten
fold excess to that of iron. AuCl₄⁻, C₄H₄O₆⁻¹, F⁻, CO₃²⁻, V₅O₆⁻², and ClO₄⁻¹ ion interfered slightly in ten fold excess
(error within 5% in the μg level).

Attempts made for the removal of interference due to
crómium(VI) and manganese(VII) proved unsuccessful. Thus for
the removal of interference due to chromium(VI), prior
separation of it, by extraction with isobutyl methyl ketone
from IV acid, was tried. But under the condition, iron was
also extracted along with chromium. Attempts to reduce
crómium(VI) to chromium(III), which does not interfere, by
using common reducing agents like sodium sulfite, hydrogen-
sulphide, ethylalcohol etc. resulted in reduction of the
iron(III) also to its ferrous state. In the case of
manganese(VII) too, attempts at its reduction with reducing agents reduced both iron and manganese at the same time. It has been observed that chromium(III) and manganese(II) did not interfere even when present in their ten fold excess (Table 2). The fact that in the dissolution of most of the minerals and alloy samples of iron, containing chromium and manganese as associated elements, barring a few exceptional cases, conversion of manganese(II) to manganese(VII) and chromium(III) to chromium(VI) by oxidation will not occur. As such, no problem is likely to arise in the determination of iron in such samples.

The method is, thus, found to be a simple, rapid and sensitive one providing a good recovery of iron in presence of equal amounts of most of the common ions.
### Table 1

Extractive spectrophotometric determination of iron

<table>
<thead>
<tr>
<th>Iron in µg Present</th>
<th>Iron in µg Found</th>
<th>Error</th>
<th>Iron in µg Present</th>
<th>Iron in µg Found</th>
<th>% Error</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>6.6</td>
<td>2</td>
<td>22</td>
<td>21.75</td>
<td>1.14</td>
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<tr>
<td>8</td>
<td>7.85</td>
<td>1.87</td>
<td>26</td>
<td>25.4</td>
<td>2.3</td>
</tr>
<tr>
<td>12</td>
<td>12.2</td>
<td>1.66</td>
<td>30</td>
<td>29.6</td>
<td>1.35</td>
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<tr>
<td>15</td>
<td>15.25</td>
<td>1.66</td>
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<td>34.4</td>
<td>1.76</td>
</tr>
<tr>
<td>18</td>
<td>17.73</td>
<td>1.4</td>
<td>38</td>
<td>37.5</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td>40.55</td>
<td></td>
<td>1.18</td>
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Table 2

Effect of diverse ions on the determination of iron (20 μg of iron was taken in each determination)

<table>
<thead>
<tr>
<th>Interfering ion added</th>
<th>Amount in (μg)</th>
<th>Iron found (μg)</th>
<th>% Error</th>
<th>Interfering ion added</th>
<th>Amount in (μg)</th>
<th>Iron found (μg)</th>
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<tbody>
<tr>
<td>Cd(II)</td>
<td>20</td>
<td>20.0</td>
<td>Nil</td>
<td>V_{NO_{3}}^{-2}</td>
<td>20</td>
<td>20.0</td>
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<tr>
<td>Cd(II)</td>
<td>200</td>
<td>20.0</td>
<td>Nil</td>
<td>V_{NO_{2}}^{-1}</td>
<td>20</td>
<td>19.6</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>20</td>
<td>20.5</td>
<td>2.5</td>
<td>V_{NO_{2}}^{-2}</td>
<td>200</td>
<td>18.0</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>200</td>
<td>21.5</td>
<td>7.5</td>
<td>CrC_{3h}^{-2}</td>
<td>20</td>
<td>25.0</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>20</td>
<td>20.0</td>
<td>Nil</td>
<td>CrC_{3h}^{-2}</td>
<td>200</td>
<td>37.0 Interfered</td>
</tr>
<tr>
<td>Sg(II)</td>
<td>200</td>
<td>20.0</td>
<td>Nil</td>
<td>F_{nt}^{-1}</td>
<td>20</td>
<td>21.5</td>
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<tr>
<td>Sn(II)</td>
<td>20</td>
<td>20.0</td>
<td>Nil</td>
<td>F_{nt}^{-1}</td>
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<td>22.5</td>
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<td>Zn(II)</td>
<td>200</td>
<td>20.1</td>
<td>0.5</td>
<td>CN_{3}^{-1}</td>
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<td>Yn(II)</td>
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<td>20.0</td>
<td>Nil</td>
<td>CN_{3}^{-1}</td>
<td>200</td>
<td>-</td>
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<tr>
<td>Yn(II)</td>
<td>200</td>
<td>20.0</td>
<td>Nil</td>
<td>C_{3h}H_{6}C_{2}^{-1}</td>
<td>20</td>
<td>20.0</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>20</td>
<td>20.0</td>
<td>Nil</td>
<td>C_{3h}H_{6}C_{2}^{-1}</td>
<td>200</td>
<td>21.0</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>200</td>
<td>20.0</td>
<td>Nil</td>
<td>C_{3h}H_{6}C_{2}^{-1}</td>
<td>20</td>
<td>19.5</td>
</tr>
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<td>Sn(III)</td>
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<td>4.5</td>
<td>VO_{3}^{-1}</td>
<td>200</td>
<td>19.0</td>
</tr>
<tr>
<td>Sn(IV)</td>
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<td>19.0</td>
</tr>
<tr>
<td>Sn(IV)</td>
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<td>12.5</td>
<td>VO_{3}^{-1}</td>
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<td>20.5</td>
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<tr>
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<td>20.0</td>
<td>Nil</td>
<td>VO_{3}^{-1}</td>
<td>20</td>
<td>20.0</td>
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<td>AlCl_{3}^{-1}</td>
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<td>21.4</td>
<td>7.0</td>
<td>VO_{3}^{-1}</td>
<td>200</td>
<td>20.0</td>
</tr>
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<td>NO_{3}^{-2}</td>
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<td>20.0</td>
<td>Nil</td>
<td>CrC_{3h}^{-1}</td>
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<td>19.4</td>
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1. H. Ossian, Pharm Centr., 13, 203, 1837.


