Spectrophotometric Determination of Iron(III) after Separation by Adsorption of its N-benzoyl-N-phenylhydroxylamine Complex on Naphthalene

MEMOIRS OF THE FACULTY OF ENGINEERING
FUKUI UNIVERSITY
VOL.27 No.2 1979

Spectrophotometric Determination of Iron(III) after Separation by Adsorption of its N-benzoyl-N-phenylhydroxylamine Complex on Naphthalene

Masatada SATAKE, Toshihiko YOKOTA and Nobusute YOSHIDA*

(Received Jul. 31, 1979)

The method is presented for the spectrophotometric determination of trace amounts of iron(III) after separation by adsorption of the complex on microcrystalline naphthalene. Iron(III) reacts with BPA to form a water-insoluble complex, which is easily adsorbed on microcrystalline naphthalene at room temperature. The mixture of complex and naphthalene is separated from aqueous solution and dissolved in dimethylformamide. The absorbance of the solution is measured at 437 nm against the reagent blank. Effects of pH, amounts of BPA and naphthalene, digestion time, standing time, shaking time and diverse foreign ions are studied. The molar absorptivity was 4.47×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$, the sensitivity of the complex as expressed by the Sandell's notation being 1.25×10^{-2} μg of copper per cm^2. Sample solution containing 50 μg of iron(III) was analyzed ten times by the recommended procedure. The mean absorbance was 0.400 with relative standard deviation of 1.25%.

1 Introduction

We have already developed a new original adsorption method "spectrophotometric determination of metals after separation by adsorption of their complexes on microcrystalline naphthalene", and this method was applied for the analysis of trace amounts of metals.

In the present study, N-benzoyl-N-phenylhydroxylamine(abbreviated as BPA) was chosen as a complexing reagent for the determination of iron(III). BPA forms a water-insoluble red complex with iron(III) at pH 3.2-8.3. This complex is adsorbed with microcrystalline naphthalene in aqueous solution. After adsorption, the resulting mixture of the complex and naphthalene is separated, dried and dissolved in dimethylformamide. The absorbance of the solution is measured at 437 nm against the reagent blank similarly prepared. The red color of this complex in naphthalene-dimethylformamide solution is very stable for a long time.

* Division of Applied Science

2 Experimental method

2.1 Reagents

Standard iron(III) solution, 5 ppm. Prepared by diluting 5 ml of Standard iron solution(1000 ppm, Wako Pure Chemical Industries Ltd., Osaka, Japan) to 1000 ml with water.

BPA solution, 0.2%. Prepared by dissolving 0.2 g of BPA in 100 ml of ethanol.

Buffer solutions were prepared from 1M acetic acid and 1M ammonium acetate solution for pH 3-6, and from 1M aqueous ammonia and 1M ammonium acetate solution for pH 8-11.

Naphthalene solution, 20%. Prepared by dissolving 20 g of naphthalene in 100 ml of acetone.

Naphthalene, acetone, dimethylformamide and all other reagents were of analytical-reagent grade, and were used without further purification.

Deionized water was used.

2.2 Apparatus

Absorption measurements were made with matched 10 mm glass cells on a Hitachi Model 200-20 spectrophotometer.

pH measurements were made with a Toa Dempa HM-5A pH meter.

The naphthalene was dried with a Tabai Model K-2 drier(Tabai Mfg. Co. Ltd. Japan).

2.3 Procedure

A series of sample solutions was prepared containing 1-12 ml of 10 ppm standard iron solution, 2.0 ml of the buffer solution(pH 5.0) and 2.0 ml of 0.2% BPA solution in about 50 ml of total volume. Mix well, and stand for 15 min at room temperature. After 3.0 ml of 20% naphthalene solution were added, the mixing solutions were shaken for 1 min vigorously. Filter them through a filter paper(Toyo Roshi Co., No 5C) placed on a filter plate in a funnel or a glass filter(No 2 or 3) when necessary. Wash with water and dry in a dryer. Then dissolve them in dimethylformamide and make up to 10 ml. Measure the absorbances of the solutions in 10 mm glass cells against the reagent blank prepared similarly.

3 Results and discussion

3.1 Absorption spectra

Figure 1 shows the absorption spectra of the reagent blank and of the iron complex in naphthalene-dimethylformamide solution resulting from taking 50 μg of iron through the procedure. The iron complex has one absorption maximum at 437 nm. At this wavelength, there is practically

no absorption due to the reagent blank, and 437 nm was therefore chosen as the most suitable wavelength.

2.2 Effect of pH

The effect of pH on the adsorption of the iron(III) complex is shown in Fig. 2. The pH measurements on the aqueous solution after adsorption were made at room temperature. The adsorption of the complex started from pH 1.8, increased sharply with increasing pH, became almost constant in the pH range 3.2-8.3 and decreased rapidly above pH 8.3. Therefore, The pH range 3.2-8.3 would seem to be most suitable.

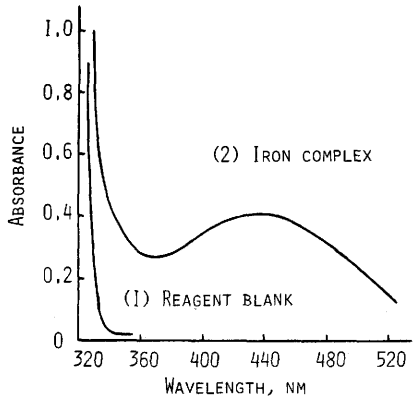

FIG.1 ABSORPTION SPECTRA OF BPA AND IRON COMPLEX IN NAPHTHALENE-DMF SOLUTION
IRON(III) : 50 μG ; PH : 5.0 ; 0.2% BPA : 2.0 ML ; DIGESTION TIME : 15 MIN ; 20% NAPHTHALENE : 3.0 ML
REFERENCE : WATER ; (1) REAGENT BLANK, (2) IRON(III) COMPLEX

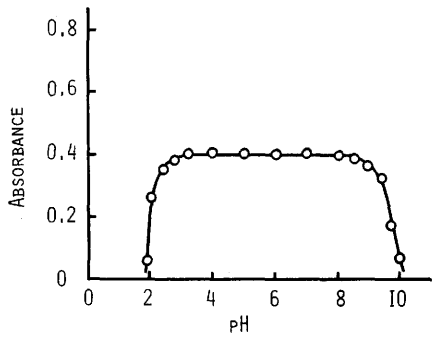

FIG. 2 EFFECT OF PH
IRON(III) : 50 μG ; WAVELENGTH : 437 NM ; 0.2% BPA : 2.0 ML ; SHAKING TIME : 1.5 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

3.3 Effect of BPA concentration and of addition of buffer solution

Various amounts of the ethanolic 0.2% BPA solution were added to the solution containing 50 μg of iron(III) and 2.0 ml of the buffer solution (pH 5.0), and the procedure was followed as given above. Figure 3 shows the variation in the measured absorbance with the reagent concentration. when volumes between 0.8 and 5.0 ml of reagent solution were used, the absorbance was effectively constant. Therefore, 2.0 ml of 0.2% solution were added. Varying the volume of the buffer solution from 0.7 to 5.0 ml at pH 5.0 did not affect the absorbance. In the present experiment, 2.0 ml of 1M buffer solution were added.

3.4 Effect of digestion time

The iron(III) complex in the solution was stood and digested at room

temperature, and the effect of digestion time on the absorbance was studied. The result is shown in Table 1. The digestion for up to 30 min gave no effect on the absorbance. Therefore, the digestion time for 15 min were selected for the absorbance measurements.

Table 1 Effect of digestion time

Digestion time min	Absorbance 437 nm
0.5	0.397
1	0.395
2	0.398
5	0.402
10	0.403
20	0.400
30	0.405

Iron(III) : 50 μg ; pH : 5.0

3.5 Effect of addition of naphthalene

Varying volumes of 20% naphthalene solution in acetone were added to the solutions containing 50 μg of iron(III) and 2.0 ml of 0.2% BPA solution at pH 5.0, and the procedure was followed. The result is shown in Fig.4. The absorbance increased slowly with increasing amount of naphthalene up to 0.6 ml, and became almost constant in the range 0.6-5.0 ml. Therefore, 3.0 ml of 20% naphthalene solution were chosen as the most suitable amount.

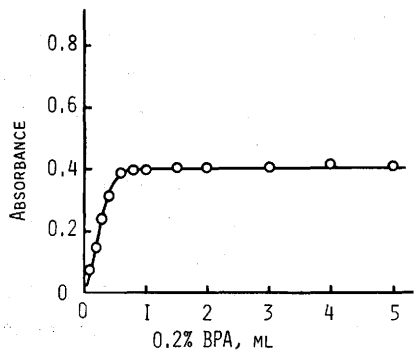

FIG. 3 EFFECT OF BPA CONCENTRATION
IRON(III) : 50 μG ; PH : 5.0 ; DIGESTION TIME : 15 MIN ; SHAKING TIME : 1.5 MIN
REFERENCE : REAGENT BLANK

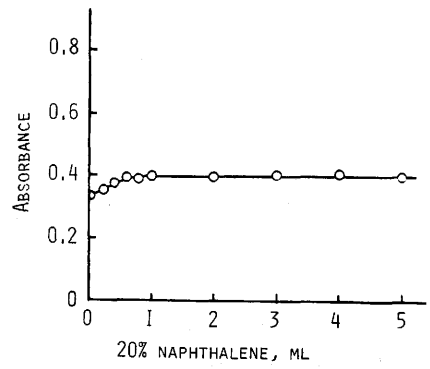

FIG. 4 EFFECT OF NAPHTHALENE CONCENTRATION
IRON(III) : 50 μG ; WAVELENGTH : 437 NM ; PH : 5.0 ; 20% NAPHTHALENE : 3.0 ML ; SHAKING TIME : 1.5 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

3.6 Effect of shaking time and standing time

Three ml of 20% naphthalene solution in acetone were added to the solutions containing the iron(III) complex, and the mixed solutions were shaken vigorously for times ranging from 0 to 300 seconds. The result is shown in Table 2. The complex was adsorbed quantitatively on microcrystalline naphthalene by vigorous shaking for 30 seconds.

The color of the complex in naphthalene-dimethylformamide solution was very stable even after standing for 50 min. The result is shown in Table 3.

Table 2 Effect of shaking time

Shaking time sec	Absorbance 437 nm
0	0.250
25	0.396
60	0.401
100	0.402
200	0.398
300	0.407

Iron(III) : 50 μg ; pH : 5.0

Table 3 Effect of standing time

Standing time min	Absorbance 437 nm
3	0.398
10	0.400
20	0.403
30	0.400
40	0.402
50	0.402

Iron(III) : 50 μg ; pH : 5.0

3.7 Effect of volume of aqueous phase

The volume of the aqueous phase was varied between 50 and 1800 ml while other factors were kept constant. The result is shown in Table 4. Though the volume of the aqueous phase does not affect the adsorption of the complex for smaller volumes,allowance must be made for larger volumes by shaking for a long time and using a larger volume of reagent solution. In this series of tests, 3.0 ml of reagent solution were taken, and the

mixed solutions were shaken for 10 minutes.

3.8 Calibration cueve

The optimum conditions described above were used and the absorbances for varying concentrations of iron(III) were measured at 437 nm against the reagent blank. The absorbances showed a linear relationship to the concentration of iron(III) in the range 6-125 μg per 10 ml of dimethylformamide. The molar absorptivity was 4.47×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$, the sensitivity being 1.25×10^{-2} μg of iron(III) for the absorbance of 0.001. Ten replicate determinations of the sample solution containing 50 μg of iron(III) gave a mean absorbance of 0.400 with a relative standard deviation of 1.25%.

3.9 Choice of solvent

Tests were made with various solvents to dissolve the mixture of the complex and the naphthalene. The complex is soluble in many organic solvents such as acetonitrile, benzene, chlorobenzene, chloroform, acetone, dioxane, toluene, xylene, etc..

3.10 Effect of diverse ions

Possible interferences were looked for by taking 50 μg of iron(III) through the procedure in the presence of various amounts of alkali metal salts and metal ions. The following species interfered : NH_4Cl(300 mg), NaCl(300 mg), Na_2SO_4(500 mg), CH_3COONa(300 mg), sodium tartrate(50 mg), Mg^{2+}(100 μg), Ni^{2+}(100 μg), Cd^{2+}(100 μg), Zn^{2+}(100 μg), Hg^{2+}(50 μg), Bi^{3+}(50 μg), Pd^{2+}(50 μg). $Na_2HPO_4 \cdot 12H_2O$, $NaH_2PO_4 \cdot 2H_2O$, Na_2CO_3, KCN, sodium citrate and EDTA gave serious interferences. The result is shown in Tables 5 and 6.

Table 4 Effect of volume of aqueous phase

Volume of aqueous phase ml	Absorbance 437 nm
50	0.405
90	0.407
120	0.387
150	0.399
180	0.397
240	0.390
300	0.385
600	0.300
1200	0.275

1800	0.205

Iron(III) : 50 μg ; pH : 5.0 ; Naphthalene : 0.6 g

Table 5 Effect of foreign alkali salts

Salts	Amount added mg	Iron(III) found μg
—	—	50.0
NH_4Cl	100	50.0
"	300	43.5
NaCl	50	50.0
"	300	44.5
$Na_2HPO_4 \cdot 12H_2O$	50	19.5
"	300	0.0
$NaH_2PO_4 \cdot 2H_2O$	50	8.0
"	300	0.0
$NaNO_3$	50	49.0
"	300	46.0
Na_2SO_4	300	50.0
"	500	41.5
Na_2CO_3	50	17.5
"	300	22.0
KCN	50	30.0
"	100	25.5
$CH_3COONa \cdot 3H_2O$	50	47.5
"	300	29.5
Sodium tartrate	50	41.0
"	300	21.0
Sodium citrate	50	4.0
"	300	0.0
Disodium EDTA	1	0.0

Iron(III) : 50 μg ; pH :5.0 ; Naphthalene : 0.6 g

Table 6 Effect of foreign metal ions

Metal ions	Ion added μg	Iron(III) found μg
—	—	50.0
Mg^{2+}	50	50.0
"	100	41.5
Ni^{2+}	50	47.0
"	100	41.0
Cd^{2+}	50	49.5
"	100	44.0
Cu^{2+}	50	50.0
"	100	50.0
Cr^{6+}	50	50.0
"	100	47.5
Ca^{2+}	50	50.0
"	100	46.0
Zn^{2+}	10	48.0
"	50	47.0
"	100	44.0
Hg^{2+}	10	47.5
"	50	44.0
"	100	41.0
Bi^{3+}	10	50.0
"	50	42.5
"	100	42.0
Pd^{2+}	10	47.0
"	50	40.5
"	100	39.0

Iron(III) : 50 μg ; pH : 5.0 ; Naphthalene : 0.6 g