Bull. Chem. Soc. Jpn., 56, 2618—2620 (1983) [Vol. 56, No. 9

Enrichment and Determination of Trace Amounts of Iron as the Colored Complex on the Thin Layer of Ion-exchange Resins

Kunio Ohzeki,* Yuhko Satoh, Yoshito Kawamura, and Tomihito Kambara

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received February 28, 1983)

A trace amount of iron was extracted as the complex with 4,7-diphenyl-1,10-phenanthrolinedisulfonic acid from aqueous solution using finely divided anion and cation exchange resins. The mixed resins were collected on a filter paper as the disk of thin layer. The colored complex in the resin phase was determined with the use of a densitometer at 540 nm. The calibration graph was linear over the range 0.1—0.5 μg of iron(II). The relative standard deviation for 0.5 μg of iron(II) in 50 ml of the test solution was 2.1% (n=5). The method was applied to the trace determination of total iron in water samples.

The concentration procedure is usually required for the spectrophotometric determination of trace amounts of ions in water samples. Although the most popular method is the extraction of colored species into a nonaqueous solvent, the utilization of solid adsorbents is of interest. For example, Wills and Sangster[1)] used Amberlite XAD-2 for the extraction of iron(II)–1,10-phenanthroline complex. The complex fixed on the resin was then eluted by a small amount of organic solvent and determined. It was possible to concentrate the iron by a factor greater than 200. Nigo *et al.*[2)] used the cation exchanger, Dowex 50W-X4, to collect the iron(II)-complex. The determination was made by the direct measurement of the resin phase absorbance using a 1-mm cell.

The combined use of finely divided anion and cation exchange resins have been reported.[3,4,5)] The colored species were collected in the thin layer of mixed resins and determined spectrophotometrically[3,4)] or densitometrically.[5)] The volume of resin phase is about 0.07 cm^3, and so it is possible to concentrate the colored species in a 50-ml sample solution by a factor greater than 700. In the present paper, the rapid extraction of iron(II)–4,7-diphenyl-1,10-phenanthrolinedisulfonate into the resin phase is studied and the results are applied to the determination of trace amounts of iron in water samples.

Experimental

Reagents. Hydrochloric acid used was of super special grade (SSG reagent, Wako). All other chemicals used were of analytical reagent grade. Deionized redistilled water was used.

Standard stock solutions (1000 ppm) of iron(II) and iron(III) were prepared by dissolving 7.021 g of ammonium iron(II) sulfate hexahydrate and 8.634 g ammonium iron(III) sulfate dodecahydrate, respectively, in 1 dm^3 of water containing hydrochloric acid. The pH of both solutions was around 1.5. Respective working solutions, 10 ppm in iron(II) and iron(III), were prepared fresh daily by dilution with diluted hydrochloric acid solution (pH *ca.* 1.5).

The reagent, 4,7-diphenyl-1,10-phenanthroline (Bathophenanthroline, abbreviated as BP; Dotite), was used as received. A 1 mM (1 M=1 mol dm^{-3}) solution was made by dissolving 33 mg of the reagent in 50 ml of ethanol and then diluting with water to 100 ml.

Disodium salt of 4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (Bathophenanthroline disulfonic acid, Na$_2$ salt, abbreviated as BPS; Dotite) was used as received. An aqueous 1 mM solution was prepared.

An aqueous 10 w/v% solution of hydroxylammonium chloride was prepared and purified by extracting the impurity iron as the BP complex into isopentyl alcohol.

Sodium acetate was dissolved in water to give 10 w/v% solution. The impurity iron was removed extraction as the BP complex in the presence of purified hydroxylammonium chloride.

Ion-exchange Resin Suspension. The macroreticular type ion-exchangers, Amberlyst 15 and A-27 (Rohm and Haas), were used in RSO_3H and $RN(CH_3)_3Cl$ forms, respectively. The cation exchange resin suspension (CRS) and the anion exchange resin suspension (ARS) were prepared according to the method already reported.[6)] The ion-exchange capacities of CRS and ARS were determined by conductometric titration with standard sodium hydroxide and silver nitrate solutions, respectively. The capacities were 11.8 μequiv. ml^{-1} for CRS and 7.00 μequiv. ml^{-1} for ARS. When a 2-ml portion of CRS is mixed with 3 ml of ARS, both resins were almost completely coagulated and quantitatively collected on a filter paper on a holder. For masking any iron present as impurity, 10 ml of 0.01 M EDTA were added to 240 ml of CRS and ARS, respectively.

Apparatus. A Toyo KG-25 filter holder was used with filter paper of No. 5B (Toyo Roshi) for preparing thin layer of the mixed resins by filtration.

The densitometer used was a Shimadzu Chromatoscanner CS-920. Numerical values corresponding to the integrated absorbance were printed out automatically. Experimental conditions were as follows; *i.e.*, wavelength 540 nm, scanparameter, x=24 mm and y=30 mm, linearizer 1. A Shimadzu spectrophotometer UV-240 was also used.

Micropipets (Finnpipett) were used for pipetting out the working solution and hydrochloric acid.

A Corning hot plate, PC-100, was used. The 100-ml beakers containing sample solutions were placed on the hot plate and covered with a 5-dm^3 beaker. Nitrogen gas was introduced in the covering beaker and samples were heated.

All glasswares were immersed overnight in 6 M nitric acid, and then rinsed thoroughly with deionized water.

Procedure. Place a sample solution, containing usually less than 0.5 μg of iron, in a 100-ml beaker. Add 100 μl of 20% hydrochloric acid and 2.0 ml of 10% hydroxylammonium chloride. Heat on the hot plate for 15 min under nitrogen atmosphere, and cool the sample to room temperature. Add 1.0 ml of 1 mM BPS solution and 2.0 ml of sodium acetate solution. Adjust the volume to 50 ml with water. The pH of final solution is 4.5. Allow the mixture to stand for 20 min and then add 2.0 ml of CRS and 3.0 ml of ARS. Stir the mixture for 5 min. Collect the resulting coagulated resins on a filter paper strip placed on the holder by suction. A disk of thin layer, 17 mm in

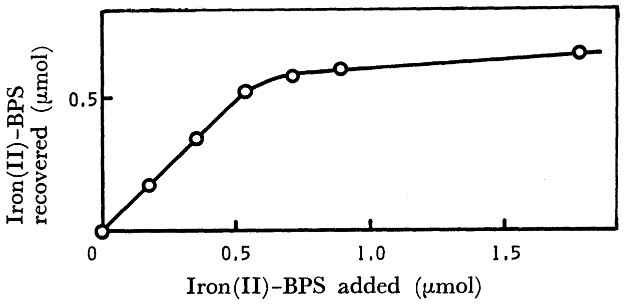

Fig. 1. Recovery of iron(II)-BPS complex on the resin mixture of 3.0 ml of ARS and 2.0 ml of CRS. Test solution 50 ml, ionic strength 0.01.

diameter and about 0.3 mm in thickness, is obtained. Keep the filter strip wet in water for 10 min, and place it on a white plastic plate fixed on a scanning board in the chromatoscanner. Measure the absorbance twice and determine the mean of duplicate values, which coincided each other within less than 0.1%.

The calibration graph was prepared using the iron(II) standard solution, the heating step being omitted. There was no significant difference between the blank values obtained with and without heating step.

Results and Discussion

Masking of Impurity Iron in CRS and ARS. The impurity in hydroxylammonium chloride, as well as in sodium acetate solution, was removed successfully by extraction as iron(II)-BP complex, but the extraction procedure could not be applied to the purification of ion-exchange resins. The use of EDTA was found to be efficient. When EDTA was previously added to ARS and CRS, the formation of iron(II)-BPS complex from the impurity in the resins was masked effectively, while the complex once formed was stable in the presence of EDTA.

Preparation of Thin Layer of Mixed Resins. In the course of 5-min stirring, the iron(II)-BPS complex was fixed on the anion exchange resin and the resin was coagulated with the cation exchanger. The resin mixture was collected on a filter paper by filtration with suction within 5 min. The stable coloration was kept for at least 3 h, when the thin layer was stored in wet in water. The absorption spectrum of the iron(II)-BPS complex was compared with that in the solution. A small shift of the maximum wavelength was observed, *i.e.*, from 533 nm in the solution to 540 nm in the resin phase.

Recovery of Iron(II)-BPS Complex. The extraction of the complex into the resin mixture of 3.0 ml of ARS and 2.0 ml of CRS was examined in the presence of 0.01 M sodium chloride to keep a constant ionic strength. Up to 0.54 μmol, the complex was quantitatively fixed on the mixed resins (Fig. 1). The recovery of 0.5 μg of iron(II) as the BPS complex on the mixed resins was also studied by varying added amounts of BPS from 0.5 to 3.5 μmol. A constant recovery was obtained over the range studied.

Calibration Graph. The least-squares regression equation for iron(II) over the range 0.1—0.5 μg was $y=5.79\times10^4x+2.58\times10^4$, where y is the integrated absorbance of the resin phase, as measured against the filter paper, and x is the amount of iron(II) in μg. The intercept at $x=0$ is due to the background absorbance of the thin layer prepared from the test solution without addition of iron(II). The mean value with the standard deviation was $(2.60\pm0.05)\times10^4$ ($n=5$) for the blank and $(5.48\pm0.03)\times10^4$ ($n=5$) for 0.5 μg of iron(II). Thus, the net value for 0.5 μg of iron(II) was $(2.88\pm0.06)\times10^4$, and the relative standard deviation was 2.1%.

Effect of Copper. As well known, 1,10-phenanthroline and the analogous compounds are selective colorimetric reagents for iron.[7] Among cations likely to be present, only the interference of a large amount of copper is reported. The recovery of 0.5 μg of iron(III) as the iron(II)-BPS complex was examined in the presence of varying amounts of copper(II).

Table 1. Effect of copper(II) on determination of iron(III)[a]

Cu(II) added (μg)	Net value of chromatoscanner absorbance for iron(II)-BPS×10⁻⁴	Recovery (%)
0	2.94	100
5	2.95	100
10	2.92	99
20	3.00	102
50	0.66	22

a) Iron(III) taken: 0.5 μg.

Table 2. Determination of total iron in water samples

Sample	Sample amount (ml)	Iron(II) added (μg)	Iron found (μg)	Iron in sample (μg)	Iron in sample (ng ml⁻¹)
Tap water					
Sep. 17, 1981	50	0.00	0.20_4	0.20_4	4.1
	50	0.10	0.30_0	0.20_0	4.0
	50	0.20	0.40_1	0.20_1	4.0
Nov. 17, 1981	50	0.00	0.07_6	0.07_6	1.5
	50	0.10	0.18_1	0.08_1	1.6
	50	0.20	0.27_9	0.07_9	1.6
Mineral	5	0.00	0.20_2	0.20_2	40.4
	5	0.10	0.30_4	0.20_4	40.8
	5	0.20	0.39_0	0.19_0	38.0

The recovery was quantitative in the presence of 20 μg of copper (Table 1). In the presence of 50 μg of copper, however, copper(I)–BPS complex is predominantly formed and the recovery of iron was suppressed.

Determination of Total Iron in Water Samples. The total iron in the tap water supplied to our laboratory from the well in our University campus was determined. After the running of water longer than 20 min, the 50-ml portions were taken. The recovery of added amounts of iron(II) was quantitative (Table 2). The iron content in a commercially available mineral water was also determined successfully.

The present method is very sensitive and only a small sample amount is required, which is especially advantageous to the determination of total iron, since the sample is easily heated without contamination from the vessel and atmosphere.

The solvent extraction method[8] requires a 200-ml sample solution and a 4-cm cuvette for the determination of iron in the ppb range as the iron(II)–BP complex. The solvent extraction process using a large volume of sample water is tedious.

References

1) R. B. Wills and D. Sangster, *Anal. Chem.*, **48**, 59 (1976).

2) S. Nigo, K. Yoshimura, and T. Tarutani, *Talanta*, **28**, 669 (1981).

3) K. Ohzeki, T. Sakuma, and T. Kambara, *Bull. Chem. Soc. Jpn.* **53**, 2878 (1980).

4) K. Matsuhisa, K. Ohzeki, and T. Kambara, *Bull. Chem. Soc. Jpn.*, **54**, 2675 (1981).

5) K. Suzuki, G-D. Park, K. Ohzeki, and T. Kambara, *Bull. Chem. Soc. Jpn.*, **55**, 3335 (1982).

6) M. Abe, K. Ohzeki, and T. Kambara, *Bull. Chem. Soc. Jpn.*, **51**, 1090 (1978).

7) O. G. Koch and G. A. Koh-Dedic, "Handbuch der Spurenanalyse 2," Auflage, Springer-Verlag, (1974), p. 696.

8) A. L. Willson, *Analyst*, **89**, 389 (1964).