Spectrophotometric Determination of Anions by Solvent Extraction with Metal Chelate Cations. XIV[1] Determination of Iodide Ions with Tris(1,10-phenanthroline)iron(II)

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Iodide was extracted from the aqueous phase into nitrobenzene in a wide pH range of 3—9 by use of tris(1,10-phenanthroline)iron(II) chelate cations and then determined spectrophotometrically at 516 mμ. Beer's law was effective up to 8.0×10^{-5} M of iodide in the aqueous phase. Standard deviation of the determination was 1.1% at 15°C. The color intensity of the extracted species in nitrobenzene was constant for at least 3 hr. The distribution ratio was 1.02 at 15°C and 0.83 at 26°C. No serious interferences by foreign anions were observed except for perchlorate, chlorate, and thiocyanate. Cations did not essentially interfere with the determination.

Iodide can be determined colorimetrically through its catalytic action, by starch-iodide reaction or as a triiodo ion.[2] However, these procedures are tedious and delicate, and the reactions involved are not very well defined.

We have previously presented, as a short communication, a new method for the spectrophotometric determination of iodide which was based on the solvent extraction with tris(1,10-phenanthroline)iron(II) chelate cations.[3] At that time, acetate buffer solution was used; which showed a relatively high reagent blank in the pH range of 4 to 5. It was later found that the absorbance of the reagent blank is negligible when phosphate buffer solution is used instead. Here, an improved method is presented together with more detailed results.

Iodide ions are well extracted into nitrobenzene over a wide pH range of 3 to 9. Determination is carried out spectrophotometrically at 516 mμ. Beer's law is effective up to 8.0×10^{-5} M of iodide in the aqueous phase. A large amount of phosphate, sulfate, nitrate, or chloride does not interfere.

Experimental

Apparatus. Spectrophotometric measurements were made with a Hitachi 139 spectrophotometer with 10 mm glass cells. Shaking was done with an Iwaki Model KM shaker. pH measurements were done with a Hitachi-Horiba H-5 pH meter. Gamma ray counting of ^{131}I was done with an Aloka Model PSM 801 γ-ray spectrometer equipped with a NaI(Tl)crystal. An incubator, Taiyo Model M-1 with 200 times/min of shaking frequency was used as a temperature controlled shaker.

Reagent. Tris(1,10-phenanthroline)iron(II) sulfate solution. A solution of 4.0×10^{-3} M was prepared with ferrous ammonium sulfate and 1,10-phenanthroline.

Standard Iodide Solution: A standard iodide solution of 1.0×10^{-1} M was prepared with potassium iodide. Standardization was made by titration with silver nitrate solution.

Radioactive Iodide Solution: A radioactive iodide solution was prepared with NaI–^{131}I from Japan Radioisotope Association.

Buffer Solution: Phosphate buffer solution of 1.0 M was prepared with potassium dihydrogen phosphate and sodium monohydrogen phosphate. pH was adjusted to the desired values with sulfuric acid or sodium hydroxide.

Solvent: Nitrobenzene, purified by vacuum distillation at 20—30 mmHg, was used. It was equilibrated with distilled water before extraction. Other solvents were of analytical grade and were used without further purification.

Procedure. *Calibration Curve*: Take 5 m*l* of iodide solution of the concentration ranging from 8×10^{-5} to 4×10^{-4} M in a 100-m*l* separatory funnel. Add 5 m*l* of the tris(1,10-phenanthroline)iron(II) sulfate solution (4×10^{-3} M) and 5 m*l* of the phosphate buffer solution to adjust the pH of the mixture to 5.5. Dilute it to 25 m*l* with distilled water. Add 10 m*l* of nitrobenzene previously equilibrated with distilled water and shake the funnel for 2 min. About 30 min after the extraction, remove the organic layer and dehydrate it with 1 g of anhydrous sodium sulfate, allowing it to stand another 10 min. Measure its absorbance at 516 mμ with the reagent blank or nitrobenzene as a reference.

Distribution Ratio: a) By means of spectrophotometry. To 15 m*l* of aqueous solution of tris(1,10-phenanthroline)iron(II) iodide prepared from the synthesized salt (1×10^{-4} M) at pH 5.5 with phosphate buffer, add 15 m*l* of nitrobenzene and extract for 10 min at a constant temperature. After extraction, measure the absorbance of the aqueous and the organic phase at 510 mμ and 516 mμ, respectively. Use water or nitrobenzene as a reference.

b) By means of radioactivity measurement. To the same aqueous solution, add a trace amount of radioactive iodide solution. Proceed the extraction as above. After the extraction, measure the radioactivity of both phases.

Results and Discussion

Absorption Spectra. The absorption spectra of an extract and a reagent blank are shown in Fig. 1. The absorption maximum of the extract was identical with that of tris(1,10-phenanthroline)iron(II) iodide salt dissolved in nitrobenzene. The extracted species was confirmed to be $\mathrm{Fe(phen)_3 \cdot I_2}$ also by the continuous variation method, where phen represents 1,10-phenanthroline.

pH. This species shows a constant absorbance when extracted from aqueous phase with a wide pH range of 3 to 9 as shown in Fig. 2, indicating that the degree of extraction is maximum in this pH range. When acetate buffer solution was used instead of phos-

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[1] Part XIII of this series: S. Hayashi, K. Kotsuji, T. Sakurai K. Kimura, and Y. Yamamoto, This Bulletin, **38**, 1494 (1965).

[2] F. Boltz, "Colorimetric Determination of Nonmetals," Interscience Publishers, New York, N. Y. (1958), p. 202.

[3] Y. Yamamoto and S. Kinuwaki, This Bulletin, **37**, 434 (1964).

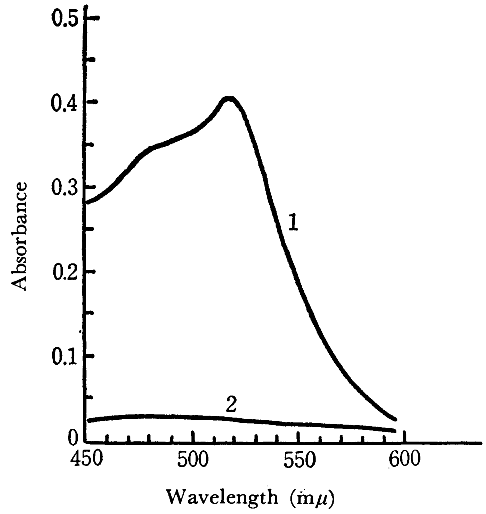

Fig. 1. Absorption spectra.
Reference: Nitrobenzene
Curve 1: Spectrum of tris(1,10-phenanthroline)iron(II) iodide in nitrobenzene extract.
[tris(1,10-phenanthroline)iron(II)] $= 8.0 \times 10^{-4}$ M
[iodide] $= 4.0 \times 10^{-5}$ M
Curve 2: Spectrum of the reagent blank.
Temperature: 15—16°C

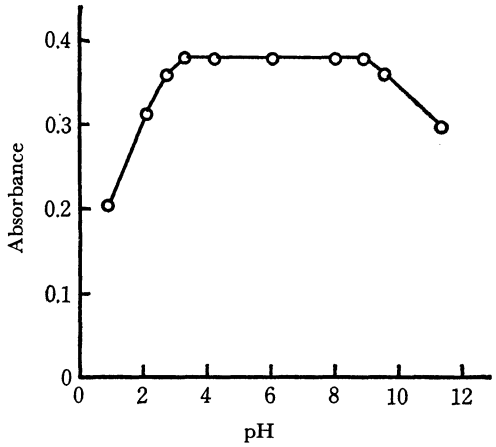

Fig. 2. Effect of pH.
[tris(1,10-phenanthroline)iron(II)] $= 8.0 \times 10^{-4}$ M
[iodide] $= 4.0 \times 10^{-5}$ M
Reference: Reagent blank
Temperature: 15—16°C

phate, the reagent blank showed a relatively high absorbance over a pH range of 4 to 6.[3,4] pH was adjusted to 5.5 throughout this experiment.

Concentration of Tris(1,10-phenanthroline)iron(II) sulfate. A constant amount of iodide (4.0×10^{-5} M) was extracted with varying amounts of the chelate. The result is shown in Fig. 3, from which it is seen that the maximum and constant extraction is attained at a mole ratio, the chelate : iodide = 4 : 1. In this experiment the ratio was kept at about 10 : 1.

Shaking Time. Shaking time of the extraction was varied from 0.5 to 30 min. No difference was observed and therefore the shaking time was fixed to 2 min for convenience.

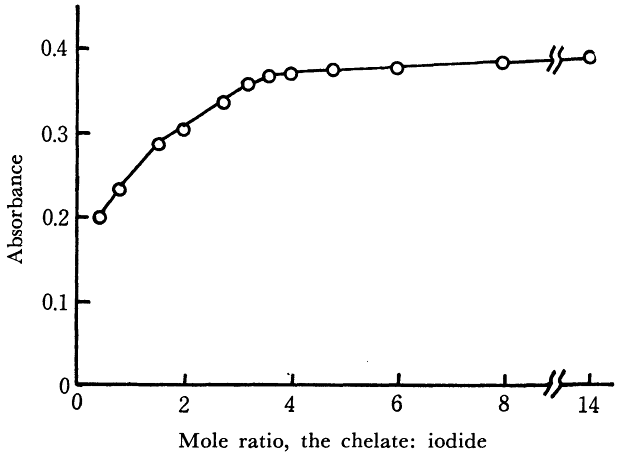

Fig. 3. Effect of the chelate concentration.
[iodide] $= 4.0 \times 10^{-5}$ M
Reference: Reagent blank
Temperature: 15—16°C

Stability of Color. Color intensity of the nitrobenzene phase was constant for 3 hr. A slight fading was observed after several hours (after 5 hr, 0.8%).

Frequency of Extraction. As shown in Table 1, the second and the third extracts still have appreciable absorbances. However, only the first extract was used in this experiment.

Table 1. Effect of frequency of extraction
(Iodide: 4×10^{-5} M, Reference: Nitrobenzene, Temp. 15—16°C.)

Number of extraction	Absorbance
1st	0.405
2nd	0.198
3rd	0.105
4th	0.053
5th	0.034
6th	0.024

Calibration Curve. The plot of absorbance of the nitrobenzene phase *versus* concentration of iodide in the aqueous phase gave a straight line up to 8.0×10^{-5} M. (*cf.* Fig. 4).

Precision. Six samples of iodide solution of 4.0×10^{-5} M were subjected to extraction. These samples gave a mean absorbance value of 0.380 against the reagent blank with a standard deviation of 0.004 or 1.1% at 15°C.

Distribution Ratio and Temperature Effect. Distribution ratio D by spectrophotometry will be expressed as:

$$D = \frac{[\mathrm{Fe(phen)_3I_2}]_o + [\mathrm{Fe(phen)_3I^+}]_o + [\mathrm{Fe(phen)_3{}^{2+}}]_o}{[\mathrm{Fe(phen)_3I_2}]_w + [\mathrm{Fe(phen)_3I^+}]_w + [\mathrm{Fe(phen)_3{}^{2+}}]_w}$$

because the synthesized salt of the formula, $\mathrm{Fe(phen)_3I_2}$, is dissolved in the aqueous phase and therefore tris(1,10-phenanthroline)iron(II) cations exist in an equivalent amount to ioide. Results were as follows: at 15°C, 1.02 and at 26°C, 0.83, *i.e.*, the lower the temperature, the more effective is the extraction. This fact is also seen in Fig. 4 where calibration curves at various temperatures are shown. The distribution

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[4] Y. Yamamoto, K. Kotsuji, S. Kinuwaki, and H. Sawamura, *Nippon Kagaku Zasshi*, **85**, 869 (1964).

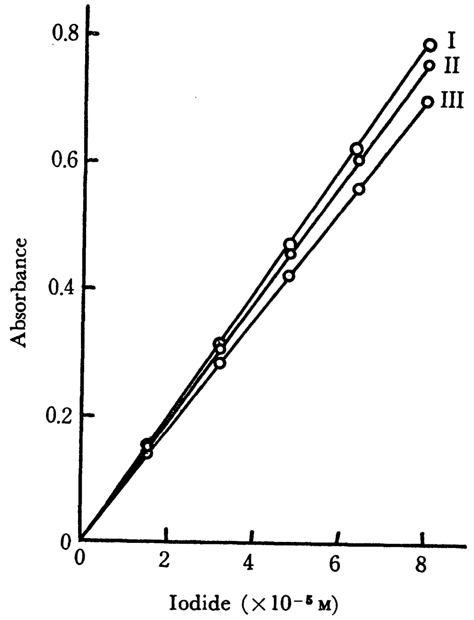

Fig. 4. Temperature effect on the calibration curve. [tris(1,10-phenanthroline)iron(II)] = 8.0×10^{-4} M
Reference: Reagent blank
I : 11°C, II : 15°C, III : 22°C

Table 2. Choice of organic solvent
(Iodide: 4×10^{-5} M. Wavelength: 516 mμ. Reference: pure solvent. Temp. 15—16°)

Solvent	Dielectric constant	Absorbance
Nitrobenzene	34.8	0.405
m-Nitrotoluene	23.8	0.134
o-Nitrotoluene	27.4	0.155
Benzene	2.3	~0
Benzonitrile	25.2	0.170
Toluene	2.4	~0
Chlorobenzene	5.6	~0
Chloroform	4.8	~0
Carbon tetrachloride	2.2	~0
Carbon disulfide	2.6	~0
Methyl-iso-butyl ketone	13.1	~0
2-Pentanone	15.4	~0
1,2-Dichloroethane	10.4	0.012
Isoamylalcohol	14.7	~0
Ethyl propionate	5.7	~0

Table 3. Effect of foreign anions
(Iodide taken: 4.0×10^{-5} M. Temp. 15—16°C)

Anion	Added as	Concentration (M)	Recovery of iodide (%)
Sulfate	Na_2SO_4	4×10^{-2}	100
Sulfate	Na_2SO_4	4×10^{-4}	100
Nitrate	$NaNO_3$	4×10^{-4}	105
Nitrate	$NaNO_3$	4×10^{-5}	100
Perchlorate	$KClO_4$	4×10^{-6}	110
Perchlorate	$KClO_4$	4×10^{-7}	100
Chloride	NaCl	4×10^{-2}	122
Chloride	NaCl	4×10^{-3}	103
Bromide	NaBr	4×10^{-3}	161
Bromide	NaBr	4×10^{-4}	100
Thiocyanate	KSCN	4×10^{-6}	108
Thiocyanate	KSCN	4×10^{-7}	100
Cyanide	KCN	4×10^{-3}	127
Cyanide	KCN	4×10^{-4}	100
Chlorate	$NaClO_3$	4×10^{-5}	113
Chlorate	$NaClO_3$	4×10^{-6}	100
Bromate	$KBrO_3$	4×10^{-3}	123
Bromate	$KBrO_3$	4×10^{-4}	100
Silicate	Na_2SiO_3	4×10^{-3}	100

Table 4. Effect of foreign cations
(Iodide taken: 4.0×10^{-5} M, Temp. 15—16°C)

Cation	Added as	Concentration (M)	Recovery of iodide (%)
Magnesium	$MgSO_4$	4×10^{-3}	97.5
Calcium	$CaSO_4$	4×10^{-3}	97.0
Strontium	$SrCl_2$	4×10^{-3}	52.7
		4×10^{-3}	107[a]
Barium	$BaCl_2$	4×10^{-3}	106
Manganese(II)	$MnSO_4$	4×10^{-3}	100
Iron(III)	$Fe_2(SO_4)_3$	4×10^{-3}	80.4
		4×10^{-3}	93.5[a]
Cobalt(II)	$CoSO_4$	4×10^{-3}	97.5
Nickel	$NiSO_4$	4×10^{-3}	100
Copper(II)	$CuSO_4$	4×10^{-3}	97.5
		4×10^{-3}	100[a]
Zinc	$ZnSO_4$	4×10^{-3}	96.0
Cadmium	$CdSO_4$	4×10^{-3}	95.5
Mercury(II)	$HgSO_4$	4×10^{-5}	0
Aluminum	$KAl(SO_4)_2$	4×10^{-3}	97.5

a) 8×10^{-3} M EDTA added.

ratio from radioactivity measurement with ^{131}I as a tracer agreed well with that from spectrophotometry. This means that *D* for iodide can be correctly estimated by measuring *D* for the chelate cations.

Choice of an Organic Solvent. Various organic solvents were tested. Of these, nitrobenzene was the most effective as shown in Table 2. Roughly saying, solvents with relatively high dielectric constants are able to extract the chelate ion pair.

Interference. *Anions*: Table 3 shows the effect of diverse anions on the recovery of iodide. Perchlorate, chlorate, and thiocyanate are easily extracted and therefore interfere with the determination even when they exist in an extremely low concentration. Bromide, cyanide, and bromate do not interfere with the determination if they are present in a concentration equal to or less than that of iodide, while as chloride can coexist several hundred times as much. Nitrate shows some effect while a large amount of sulfate and phosphate (used as buffer) shows none.

Cations: Table 4 shows the effect of diverse cations on the recovery of iodide. Almost any metals tested do not interfere. Mercury(II) that reacts with iodide interfere seriously. The interference of strontium seems inexplicable. Ferric ions form hydroxide at this pH. However, these interferences are easily eliminated by use of excess EDTA except for mercury(II).