A New Colorimetric Determination of Iodide Ions by Solvent Extraction with the 1, 10-Phenanthroline-Iron(II) Complex

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This study presents a new method for the determination of iodide ions by solvent extraction. We have found that a colored 1, 10-phenanthroline-iron(II) chelate cation was extractable into nitrobenzene from aqueous solution when a small amount of iodide was present. Figure 1 shows the absorption spectra of the extracts against nitrobenzene used as a reference. The extractions were carried out from aqueous solutions containing the phenanthroline-iron(II) complex in an acetate buffer (pH 4.5). Curve 1 is a spectrum of the extract with iodide ions, while curve 2 is that of the extract when iodide is absent. It is shown that when the concentration of acetate ion is quite high, the chelate cation is also extractable into nitrobenzene, but when a small amount of iodide is present, the chelate cation is much more extractable into the organic layer. The results suggest that it is possible to determine the quantity of iodide ions by solvent extraction with the chelate cation, using the reagent blank solution as a reference.

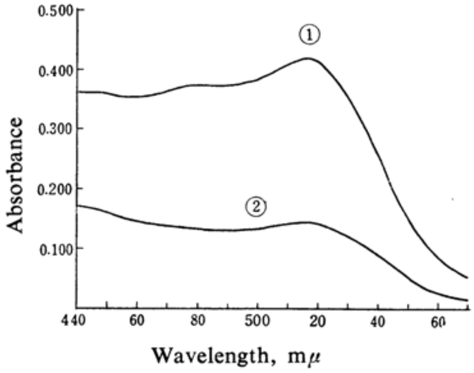

Fig. 1. Absorption spectra.

Water phase	Phenanthroline	8×10^{-4}M
	Fe^{2+}	2×10^{-4}M
	Acetate	0.24M
	I^-	1.7×10^{-5}M
	pH	4.5

① Extracts by nitrobenzene with iodide ion.
② Extracts by nitrobenzene without iodide ion.
Reference: Nitrobenzene

The absorbance maximum of the chelate cation in the organic layer is 516 mμ. The maximum of the chelate cation in an aqueous solution is 510 mμ, which coincides with the value of the literature.[1] This red shift of the spectrum in the organic layer may be due to the effect of the association between the chelate cations and iodide ions in such a polar solvent as nitobenzene.

The percentage of the extraction of iodide ions was about 90%. This was determined by the radiochemical technique using radioisotope I-131 (NaI) as a tracer. From the above findings, it may be presumed that the chemical form of the extracted species is $[Fe(phen)_3]^{2+}\cdot(I^-)_2$.

Besides nitrobenzene, various organic solvents, such as chloroform, 1, 2-dichloroethane, cyclohexanone, chlorobenzene, and benzene, were tested for the extraction. However, the associated species between the phenanthroline-iron(II) complex and iodide ions was not extractable into such a solvent.

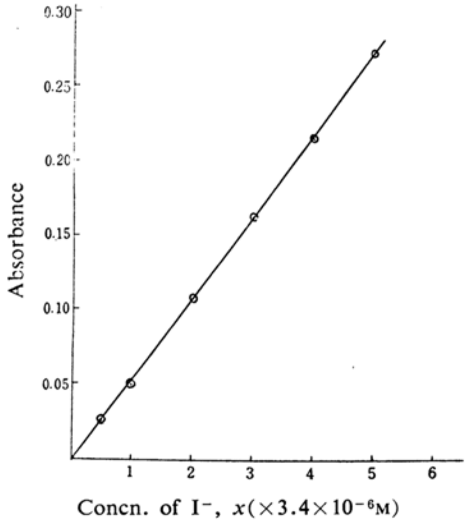

Fig. 2. Calibration curve at 516 mμ.

Water phase	Phenanthroline	8×10^{-4}M
	Fe^{2+}	2×10^{-4}M
	Acetate	0.24M
	I^-	$3.4\times10^{-6}\times x$
	pH	4.5
	Reference	Reagent blank

To obtain an optimum conditions for the determination of iodide ions, various factors were studied: the effects of the concentration of iron(II) ions (as ferrous ammonium sulfate), phenanthroline, the pH of the solution, the stability of the color, the shaking time, and the presence of diverse ions. The recommended procedure for the calibration curve (Fig. 2) is as follows:

Two milliliters of the 1, 10-phenanthroline solution (1×10^{-2}M), 1.0 ml. of the ferrous ammonium sulfate solution (5×10^{-3}M), 2 ml. of the sodium acetate buffer solution (3M, pH 4.5) and varying amounts of the standard sodium iodide solution (8.5×10^{-5}M; 0.5∼5.0 ml.) are mixed and diluted to 25 ml. with distilled water. Then 10.0 ml. of purified nitrobenzene is added. After the mixture has been shaken for 20 min., and after the organic layer has been transferred to a glass flask containing 1 g. of anhydrous sodium sulfate, the transparent solution is transferred into a 10.0 mm. cell through folded filter paper. The absorbance of the solution is measured at 516 mμ using the reagent blank solution as a reference. As is shown in Fig. 2, Beer's law is followed in the range of $1\times10^{-6}\sim5\times10^{-5}$ M of iodide ions.

When a considerable amount of chloride (about 100 times that of iodide) is present, the determination of iodide is not interfered with, but the presence of the same amounts of perchlorate or thiocyanate as iodide gives a considerable positive error.

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[1] M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **14**, 825, 931 (1942).