NOTES

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Spectrophotometric Determination of Iodide Ions by Solvent Extraction with Neutral Red[1]

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Many investigations have been made on the spectrophotometric determination of iodide ions. Although the catalytic method[2] and diphenylcarbazone-mercury(II) method[3] are sensitive, they are influenced by the changes in temperature or the presence of bromide ions.

This paper deals with a new spectrophotometric method for iodide ions, which is based on a solvent extraction of the ion-pair formed between the colored neutral red cation and colorless iodide ion. The method has a greater sensitivity than that in which methylthymol blue - mercury(II),[4] diethyldithiocarbamate-silver(I)[5] or 1,10-phenanthroline-iron(II)[6] complex, are employed.

Experimental

Apparatus and Reagents. Absorbance measurements were made with a Shimadzu Beckman Model QR-50 spectrophotometer with matched 1 cm quartz cells. An Iwaki Model KM shaker was used for extraction.

Potassium iodide of guaranteed grade was dissolved in deionized water; it was then standardized according to Volhard's method. The working standard solutions were obtained by diluting this solution. The neutral red (NR) solution of 2×10^{-3}M was prepared by dissolving NR (guaranteed grade) in 0.01N sulfuric acid. The citrate buffer solution of 0.2M was made from sodium citrate and dilute sulfuric acid.

Procedure. 2—10 m*l* of sample solutions containing less than 5×10^{-5}M of iodide ions were placed in separatory funnels. 5 m*l* of the buffer solution (pH 3) and 5 m*l* of the NR solution were then added. The solution was diluted to 25 m*l* with water. After adding 10 m*l* of nitrobenzene, the contents were mixed thoroughly by means of a shaker for about 2 min. The nitrobenzene layer were drawn off into glass tube equipped with a glass stopper containing about 1 g of anhydrous sodium sulfate, and shaken to remove droplets of water. The absorbance of the extract was measured at 552 mμ against a reagent blank.

Results

Figure 1 shows the obtained visible absorption spectra of extracts. The absorbance maximum of the extracts was at 552 mμ. From pH 7 to 11 the red color was not formed in the nitrobenzene layer. The optimum pH was 2—4. Of the solvents such as chloroform, isoamyl alcohol, nitrobenzene, methyl isobutyl ketone *n*-hexane, ethyl acetate, benzene, and ether, only nitrobenzene can extract the ion-pair consisting of NR and iodide ion. 0.01—0.08M citrate used as a buffer had no influence on the absorbance of the extract. Maximum

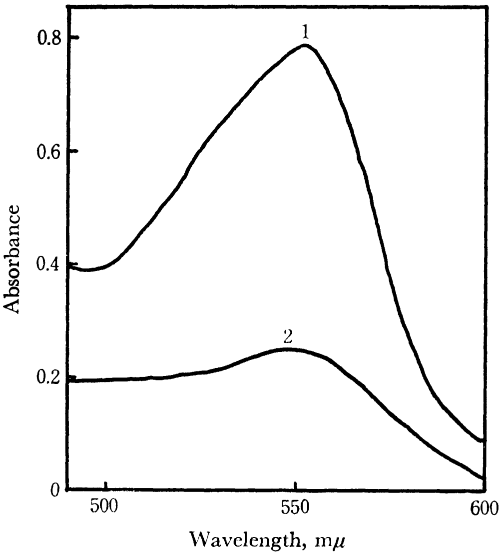

Fig. 1. Absorption spectra
1: Spectrum of organic phase extracted from the aqueous solution (25 m*l*) contained 1.6×10^{-5}M iodide.
2: Reagent blank
Reference: Nitrobenzene

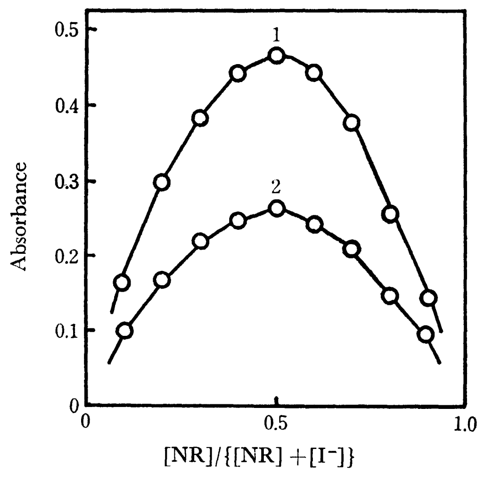

Fig. 2. Continuous variations plots.
[NR]+[I$^-$]: 8×10^{-5}M
1: 552 mμ, 2: 510 mμ
Reference: Reagent blank

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[1] Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

[2] I. Iwasaki, S. Utsumi, and T. Osawa, This Bulletin, **26**, 108 (1953).

[3] T. Okutani, *Nippon Kagaku Zasshi*, **88**, 737 (1967).

[4] T. Nomura and S. Komatsu *ibid.*, **90**, 168 (1969).

[5] S. Komatsu and T. Nomura, *ibid.*, **88**, 1164 (1967).

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

color development in the nitrobenzene layer required about a 10-fold molar excess of NR to iodide ion. Variation of room temperature 14—24°C had no measurable effect. Full color development took about 1 min shaking. The red color of the extract remained stable for 2 hr.

In order to investigate the structure of the extracted species the method of continuous variations was employed. As shown in Fig. 2, the resulting curves have a maximum at 0.5 mol fraction of NR, indicating a 1 to 1 NR - iodide ion ratio.

Calibration and Foreign Ions. The system followed Beer's law over the range of 4×10^{-6}—2×10^{-5}M of iodide ions, with molar absorptivity of 3.25×10^4 mol^{-1}·cm^{-1} liter in the aqueous solution. Experiments with ten identical samples, each with a final iodide concentration of 1.6×10^{-5}M, gave the mean absorbance 0.520, with a standard deviation of 0.005 absorbance unit.

The effect of foreign anions was studied by adding solutions of their sodium or potassium salts. Tolerance for a foreign ion was taken as the largest amount that could be present and give an absorbance differing by no more than 0.025 from that produced by iodide alone. Tolerances are shown in Table 1. Halogens and cyanide did not interfere.

TABLE 1. EFFECT OF FOREIGN IONS

Ion	Tolerance(M)	Ion	Tolerance(M)
Br^-	5×10^{-3}	HCO_3^-	5×10^{-3}
BrO_3^-	1×10^{-3}	$H_2PO_4^-$	5×10^{-3}
Cl^-	5×10^{-3}	IO_3^-	1×10^{-6}
ClO_3^-	1×10^{-6}	NO_2^-	5×10^{-5}
ClO_4^-	1×10^{-7}	NO_3^-	2×10^{-5}
CN^-	5×10^{-3}	SCN^-	2×10^{-7}
CH_3COO^-	5×10^{-3}	SO_4^{2-}	5×10^{-3}
F^-	5×10^{-3}	$S_2O_3^{2-}$	1×10^{-4}

Iodide ion: 1×10^{-5}M

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