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The Spectrophotometric Determination of Anions by Solvent Extraction with Metal Chelate Cations. V.[*1] Thiocyanate with Tris(1,10-phenanthroline)iron(II) Chelate

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A number of methods have been reported on the determination of thiocyanate. Aldridge[1] and Baker *et al.*[2] proposed colorimetric methods with a pyridine-benzidine mixture, both of which require quite tedious procedures. Kruse and Mellon[3] used copperpyridine as a color developer, the reaction mechanism of which is still obscure. Winkhaus and Uhrig[4] presented a spectrophotometric method by solvent extraction with di-π-cyclopentadienyltitanium(IV) which, though simple and sensitive, is effective only in a very narrow pH range in the acidic media. Koh and Iwasaki[5] recently reported another spectrophotometric method based on solvent extraction with methylene blue which attained very high sensitivity and was yet influenced to some extent by the reagent concentrations used in the experiment.

Here, we present a new and consistent method for the determination of a small amount of thiocyanate anions, in which thiocyanate as low as 2×10^{-6} in molar concentration was extracted from aqueous solution into nitrobenzene as tris(1,10-phenanthroline)iron(II) thiocyanate and determined spectrophotometrically.

Experimental

All the reagents used in this experiment were of analytical reagent grade and a Hitachi 139 spectrophotometer with 10 mm glass cells was used for measurement.

Recommended Procedure. Take 5 m*l* of thiocyanate solution of concentration ranging from 1×10^{-5} to 2×10^{-4} M in a 50 m*l* beaker. Add 5 m*l* of 0.02 M 1,10-phenanthroline solution, 5 m*l* of 5×10^{-3} M iron(II) solution prepared from Mohr's salt and 5 m*l* of phosphate buffer solution to adjust the pH of this mixture to 5—10. Transfer this into a separatory funnel and dilute to 25 m*l* with distilled water.

Add 10 m*l* of nitrobenzene previously equilibrated with water and shake the funnel for about 5 min. About 30 min after extraction, remove the organic layer and dehydrate with anhydrous sodium sulfate, allowing the mixture to stand another 10 min. Measure the absorbance of the organic phase at 516 mμ with the reagent blank as a reference.

Results and Discussion

The absorption spectrum of the extract is shown in Fig. 1. The absorption maximum was identical with that of tris(1,10-phenanthroline)iron(II) thiocyanate salt dissolved in nitrobenzene. The chemical formula of the extracted species was confirmed to be $[Fe(phen)_3](NCS)_2$ also by continuous variation method, where phen represents 1,10-phenanthroline. This species shows a constant absorbance when extracted from aqueous phase with a wide pH range of 5 to 10, indicating that the degree of extraction was maximum in this pH range. The percentage of the extraction was found to be 52% (*i. e.*, $D=2.7$) by referring the absorbance of the extract to that of a standard solution prepared by dissolving crystalline $[Fe(phen)_3](NCS)_2$ in nitrobenzene. The color was stable for about three hours before slight fading was observed.

Increasing the quantity of tris(1,10-phenanthroline)iron(II) against that of thiocyanate did not affect the degree of extraction, provided the former was 15 times more concentrated than the latter.

[*1] Part IV of this series: Y. Yamamoto, K. Kotsuji, S. Kinuwaki and H. Sawamura, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **85**, 59 (1964).

1) W. N. Aldridge, *Analyst*, **69**, 262 (1944).

2) M. O. Baker, R. A. Foster, B. G. Post and T. A. Hiett, *Anal. Chem.*, **27**, 448 (1955).

3) J. W. Kruse and M. G. Mellon, *ibid.*, **25**, 446 (1953).

4) G. Winkhaus and H. Uhrig, *Z. Anal. Chem.*, **200**, 14 (1964).

5) T. Koh and I. Iwasaki, This Bulletin, **40**, 569 (1967).

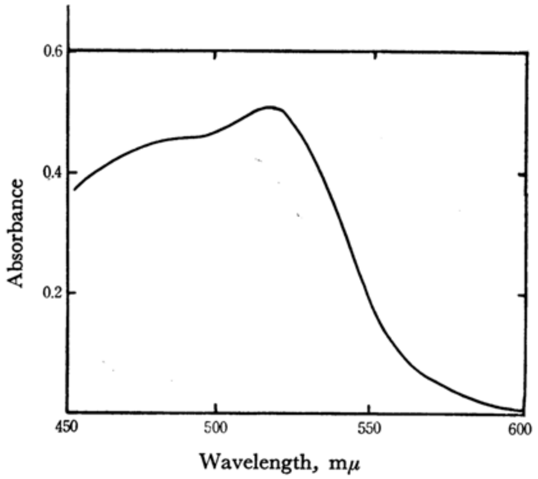

Fig. 1

Fig. 1. Absorption Spectrum of Tris(1,10-phenanthroline)iron(II) thiocyanate in Nitrobenzene Extract.
Tris(1,10-phenanthroline)iron(II) concentration $= 1.0 \times 10^{-3}$M
Thiocyanate concentration $= 4.0 \times 10^{-5}$M
Extraction was done according to the recommended procedure.
Reference : Reagent Blank.

Thus, the tris(1,10-phenanthroline)iron(II) concentration was kept at least 25 times in excess throughout the experiment.

A plot of absorbance in nitrobenzene phase *vs.* thiocyanate concentration in aqueous phase gave a linear relationship over the range of 2×10^{-6} to 4×10^{-5} M thiocyanate. As for the interference of diverse ions, metals highly reactive with thiocyanate, for example, cobalt, nickel, zinc or copper caused comparatively high negative errors when present in amounts equal to the thiocyanate concentration. Sodium, calcium, magnesium and manganese had negligible effects, even when 100 times the amount of thiocyanate was present. Perchlorate, as previously reported,⁶⁾ was the most extractable species and therefore its interference was serious. As to other anions, iodide and nitrate form ion pairs with tris(1,10-phenanthroline)iron(II) and therefore produce positive errors, while bromide, chloride, sulfate and phosphate had no appreciable effects even when present in considerable amounts, as may be seen in Table 1.

TABLE 1. EFFECT OF DIVERSE ANIONS[*2]

Anion added as sodium salt	Concentration M	Relative error %
F^-	4×10^{-2}	0
Cl^-	2×10^{-3}	0
Br^-	2×10^{-4}	+10.8
I^-	2×10^{-5}	+69.5
NO_3^-	2×10^{-5}	+11.6
SO_4^{-2}	2×10^{-3}	+1.0
$H_2PO_4^-$	2×10^{-3}	0

[*2] All the solutions are 2×10^{-5} M in thiocyanate concentration.

The interference of some cations may be easily masked with EDTA, but the interfering anions should be separated prior to the extraction of thiocyanate by proper methods like ion exchange.

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6) Y. Yamamoto, K. Kotsuji, S. Kinuwaki and H. Sawamura, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **85**, 59 (1964).