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The Spectrophotometric Determination of Anions by Solvent Extraction with Metal Chelate Cations. XLI.*1 Indirect Determination of β-Hydroxynaphthoic Acid by Atomic Absorption Spectrophotometry

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In atomic absorption spectrophotometry, a hollow cathode lamp which emits the bright spectral lines of the element to be determined is generally used as a light source. Hence, organic compounds do not lend themselves directly to determination by conventional atomic absorption methods.

The indirect determination of some organic compounds can, however, be readily performed with this analytical tool. In our previous papers, such applications have been reported in the determination of phthalic acid[1,2] and pentachlorophenol[3]; these methods were based on the solvent extraction of ion-pairs stoichiometrically formed between the anion of the organic acid and the cationic metal chelate, such as bis(neocuproine)copper(I) or tris-(1,10-phenanthroline)iron(II), and on the subsequent determination of the metal concentration in the extracts by atomic absorption spectrophotometry, the results being related quantitatively to the associated organic compound. In connection with these investigations, this study was undertaken to establish a method for the determination of β-hydroxynaphthoic acid (3-hydroxy-2-naphthoic acid), which has until now been produced through Kolbe's reaction of β-naphthol, for industrial use, mainly as an intermediate of dyestuffs. The present procedure involves the selective extraction of tris(1,10-phenanthroline)nickel(II) β-hydroxynaphthoate into nitrobenzene, followed by the measurement of the nickel concentration in the extract by atomic absorption spectrophotometry as a function of the amount of β-hydroxynaphthoic acid initially present in the aqueous phase. The presence of β-naphthol, which has been well known as a main contaminative substance in the process of manufacturing β-hydroxynaphthoic acid, did not interfere with the determination.

Experimental

Apparatus. The atomic absorption was measured with a Hitachi Model EPU-2 spectrophotometer and a Hitachi Model 0420 atomic absorption attachment equipped with a nickel hollow cathode lamp. An air-acetylene flame was burned with a water-cooled 9-cm slot burner. The shaking for the extraction was carried out by means of an Iwaki Model KM shaker.

Reagents. All the solutions were prepared from analytical reagent-grade chemicals. A stock solution of β-hydroxynaphthoic acid (1.0×10^{-2} M) or β-naphthol (1.0×10^{-2} M) was prepared by dissolving 0.941 g of β-hydroxynaphthoic acid or 0.721 g of β-naphthol in 2 m*l* of a 6N sodium hydroxide solution and a small volume of water, and then by diluting the mixture to 500 m*l* with water. These solutions were diluted to an appropriate concentration for the experiment. A phenanthroline-nickel(II) sulfate solution (1.0×10^{-2} M) was prepared by dissolving 6.343 g of 1,10-phenanthroline ($C_{10}H_8N_2\cdot H_2O$) and 0.281 g of refined nickel sulfate ($NiSO_4\cdot7H_2O$) to a volume of 1000 m*l* with water.

Procedure. Ten milliliters of the phenanthroline-nickel(II) sulfate solution, 5m*l* of a phosphate buffer solution (1/15 M, pH 6—7), and 4 m*l* of the β-hydroxynaphthoic acid solution (2.0×10^{-3} M) were placed in a 100-m*l* separatory funnel, and then the aqueous-phase volume was adjusted to 25 m*l* with water. After 10 m*l* of nitrobenzene had been poured in, the funnel was shaken for 1 min. It was left still for about 20 min after the extraction, and then the organic phase was taken out and dried with 1 g of anhydrous sodium sulfate. The absorption due to nickel in the organic phase was then determined by the use of the atomic absorption spectrophotometer against a reagent blank used as a reference, and expressed as the initial concentration of β-hydroxynaphthoic acid in the aqueous phase. The instrument-operating conditions were as follows: a wavelength of 2320Å, slit-width of 0.20 mm, and a lamp current of 15 mA (nickel lamp). The flow rates of gases for the air-acetylene flame were 8.0 *l*/min of air and 1.5 *l*/min of acetylene. The burner height was adjusted to make the light beam pass 6 mm above the tip of the burner.

Results and Discussion

Atomic Absorption of Nickel. The effects of the variation in the composition of the air-acetylene mixture on the nickel absorption in the organic extract were studied. The absorption was nearly constant when the air-flow rate was set at a constant value, although the sensitivity was enhanc-

*1 Part XL: Y. Yamamoto, N. Okamoto, and E. Tao, *Anal. Chim. Acta*, **69** (1969), in press.

1) T. Kumamaru, Y. Hayashi, N. Okamoto, E, Tao and Y. Yamamoto, *Anal. Chim. Acta*, **35**, 525 (1966).

2) T. Kumamaru, *ibid.*, **43**, 19 (1968).

3) Y. Yamamoto, T. Kumamaru and Y. Hayashi, *Talanta*, **14**, 611 (1967).

ed with an increase in the air-flow rate. For convenience, the gas-flow rates were adjusted to 8.0 *l*/min of air and 1.5 *l*/min of acetylene in subsequent work. Under these flame conditions, the highest sensitivity was obtained when the burner was so positioned that the radiation from the light source passed through the base of the flame 5—6 mm above the tip of the burner.

Extraction of β-Hydroxynaphthoic Acid with Phenanthroline-Nickel(II) Chelate. Among various commercially-available organic solvents tested for the extraction, nitrobenzene was found to be the most effective extractant for phenanthroline-nickel(II) β-hydroxynaphthoate. Moreover, nitrobenzene is a suitable solvent for atomic absorption spectrophotometry because it provides a stable flame during the combustion and a higher sensitivity of measurement. The extraction efficiency was estimated by extracting the ion-pair with successive 10 m*l* portions of nitrobenzene. It was found that 92% of β-hydroxynaphthoate was extracted in a single pass according to the procedure. Variations in the shaking time showed that shaking for longer than 0.5 min did not improve the extraction. The effect of the pH on the extraction is shown in Fig. 1.

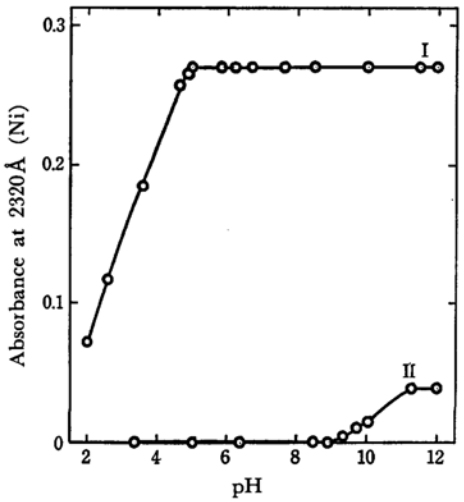

Fig. 1. Effect of pH on the extraction.
Concentration of aqueous phase: 3.2×10^{-4} M
I β-Hydroxynaphthoic acid, II β-Naphthol

The degree of the extraction of β-hydroxynaphthoate is at its maximum and is constant when the pH is held greater than 5, while β-naphtholate is only slightly extracted above pH 9. Therefore, when the method is, for instance, applied to the determination of β-hydroxynaphthoic acid in the industrial process, the pH should be in the 5—9 range in order to suppress the extraction of β-naphthol, which might contaminate the sample.

The effect of the concentration of phenanthroline-nickel(II) sulfate on the extraction of β-hydroxynaphthoate was also investigated. The absorbance of the nitrobenzene phase approached a limit when the chelate concentration was more than 1.6×10^{-3} M and when the β-hydroxynaphthoic acid concentration was kept at 3.2×10^{-4} M in the aqueous phase. Since at least a 5-fold excess (molar) of the phenanthroline chelate over β-hydroxynaphthoic acid was necessary for quantitative extractions, we decided for the sake of convenience to keep the chelate concentration at 4.0×10^{-3} M.

Calibration Curve. A plot of the absorbance due to nickel *vs.* the concentration of β-hydroxynaphthoic acid was obtained according to the procedure using varying amounts (1—5 m*l*) of the standard β-hydroxynaphthoic acid solution (2.0×10^{-3} M). As is shown in Fig. 2, this plot gives a linear relationship in the range from 8×10^{-5} to 4×10^{-4} M of β-hydroxynaphthoic acid initially present in the aqueous phase.

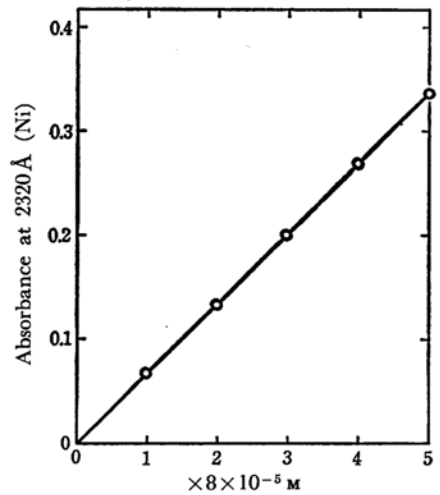

Fig. 2. Calibration curve.

Composition of Extracted Species. The continuous variation plots obtained by the atomic absorption spectrophotometric method were made in order to confirm the composition of tris (1,10-phenanthroline)nickel(II) β-hydroxynaphthoate. These plots suggested that a 1 : 2 associated ion-pair formed between the tris (1,10-phenanthroline)nickel(II) cation and the univalent anion of β-hydroxynaphthoic acid is extracted into nitrobenzene.