The Spectrophotometric Determination of Anions by Solvent Extraction with Metal Chelate Cations. VII.* A New Method for the Determination of Pentachlorophenol

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In the course of our study of the solvent extraction of an anion with a metal chelate cation,[1] it has been observed that not only inorganic anions, such as iodide, perchlorate and tetra-iodo-mercury(II) or cadmium, but also organic anions, such as trichloroacetate, or pentachlorophenolate (PCP), can be extracted into an organic solvent as nitrobenzene if the aqueous solution contains an excess of phenanthroline or dipyridyl iron(II) chelates cations.

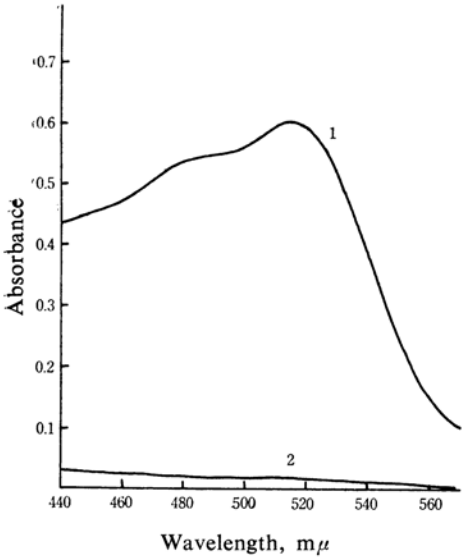

Fig. 1. Absorption spectra (reference: nitrobenzene).

Curve 1: Spectrum of organic phase extracted from the aqueous solution (25 ml.) containing $[Fe(phen)_3]$ $(2\times10^{-4}$ M), borax $(1\times10^{-2}$ M) and PCP $(4\times10^{-5}$ M), pH 10.0.

Curve 2: Spectrum of organic phase extracted from the aqueous solution (25 ml.) containing $[Fe(phen)_3]$ $(2\times10^{-4}$ M), borax $(1\times10^{-2}$ M), but PCP is absent, pH 10.0.

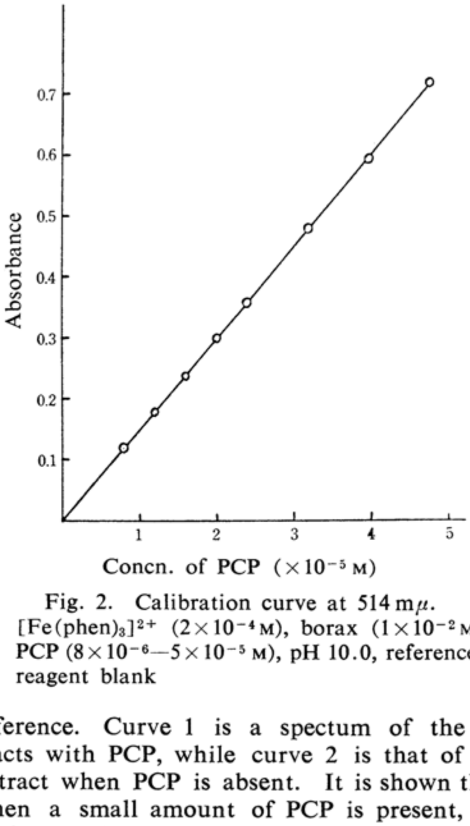

Fig. 2. Calibration curve at 514 mμ. $[Fe(phen)_3]^{2+}$ $(2\times10^{-4}$ M), borax $(1\times10^{-2}$ M), PCP $(8\times10^{-6}$—5×10^{-5} M), pH 10.0, reference: reagent blank

This study will present a method for the determination of PCP based on solvent extraction with the tris-phenanthroline iron(II) chelate. Figure 1 shows the absorption spectra of the extracts against nitrobenzene as a reference. Curve 1 is a spectum of the extracts with PCP, while curve 2 is that of the extract when PCP is absent. It is shown that, when a small amount of PCP is present, the chelate cation is quite extractable into the organic layer. The absorbance maximum of the associated species, which may be assumed to be $[Fe(phen)_3][PCP]_2$, is found at 514 mμ. A maximum extraction is obtained in the range of pH 6.0—12.0, when the molar concentration of the chelate is kept five times that of PCP. The recommended procedure for the calibration curve is as follows.

Mix 5 ml. of a tris-phenanthroline-iron(II) sulfate solution $(1\times10^{-3}$ M), 5 ml. of a borax buffer solution $(5\times10^{-2}$ M, pH 10.0), and varying amounts of the standard PCP solution, and then dilute to 25 ml. with distilled water. Shake the solution with 10.0 ml. of nitrobenzene (3 min.). Transfer the organic layer to a flask containing 1 g. of anhydrous sodium sulfate, and measure the absorbance at 514 mμ

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* VI: K. Kotsuji, This Bulletin, **38**, 402 (1965).

[1] Y. Yamamoto et al., ibid., **37**, 434, 594, 785 (1964).

using a reagent blank as a reference. Beer's law is followed in the range from 8×10^{-6} to 5×10^{-5} M. The presence of diverse ions, such as chloride, phosphate, sulfate and nitrate does not interfere with the determination, even when their amounts are about 1000 times that of PCP, but the same amount of tetrachlorophenol as that of PCP gives a slight positive error.

Although several methods,[2-4] based on the colorimetric estimation of the product obtained by the oxidation of PCP, have recently been reported, the method proposed here is based on a different mechanism of the color development and has a higher sensitivity and a better accuracy.

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