A New Colorimetric Determination of Nitrate Ions by Solvent Extraction with Crystal Violet

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In the course of our study[1] of the solvent extraction of anions, it was found that nitrate ions can be extracted into chlorobenzene when the aqueous solution contains an excess of crystal violet and that there is a linear relationship between the color intensity of the organic phase and the concentration of the nitrate ions.

Figure 1 shows the absorption spectra of crystal violet; curve 1 is a spectrum of the extract when nitrate ions are absent, while curve 2 is that of the extract with nitrate ions. The crystal violet was extracted with chlorobenzene from the aqueous solution at pH 6.0 buffered with phosphate. It was thus shown that, when a small amount of nitrate ions is present, the cation of crystal violet is quite extractable into the organic layer. The maximum of absorbance is found at 595 mμ in the organic phase, but in the aqueous phase the maximum is slightly shifted to 591 mμ (curve 3). A maximum extraction is obtained in the range of pH 5.0∼7.0, when the molar concentration of the dyestuff is held at the concentration of 10^{-4} M. The recommended procedure for the calibration curve is as follows.

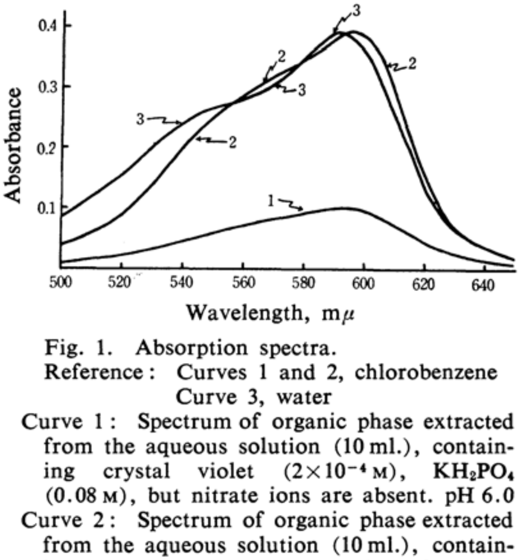

Fig. 1. Absorption spectra.
Reference: Curves 1 and 2, chlorobenzene
Curve 3, water
Curve 1: Spectrum of organic phase extracted from the aqueous solution (10 ml.), containing crystal violet (2×10^{-4} M), KH_2PO_4 (0.08 M), but nitrate ions are absent. pH 6.0
Curve 2: Spectrum of organic phase extracted from the aqueous solution (10 ml.), containing the same component as that of curve 1 and nitrate ions (2×10^{-5} M). pH 6.0
Curve 3: Spectrum of the aqueous solution of crystal violet (4×10^{-6} M). pH 6.0 (KH_2PO_4: 0.08 M)

Mix 5 ml. of the crystal violet chloride solution (1×10^{-3} M), 2 ml. of a phosphate buffer solution (1 M, pH 6.0) and various volumes of the standard nitrate solution (5×10^{-5} M). Dilute to 25 ml. with distilled water. Take the aliquot (10.0 ml.) into a separatory funnel. Shake the solution with 10.0 ml. of chlorobenzene for 5 min. Transfer the organic layer

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

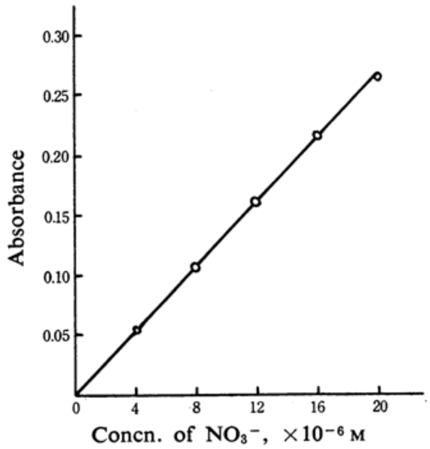

Fig. 2. Calibration curve at 595 mμ.
Reference: Reagent blank

$$\text{Water phase}\left\{\begin{array}{l}\text{Crystal violet } 2\times10^{-4}\,\text{M}\\ KH_2PO_4\ 0.08\,\text{M}\\ NO_3^-\ x\times10^{-6}\,\text{M}\\ \text{pH } 6.0\end{array}\right.$$

into the cell, and measure the absorbance at 595 mμ using a reagent blank as a reference. Beer's law is followed in the range of $4\times10^{-6}\sim2\times10^{-5}$ M. The presence of diverse ions, such as phosphate and sulfate, does not interfere with the determination, even when they are present in amounts 1000 times that of the nitrate. Chloride give rise to a slight positive error when it exists in an amount more than ten times that of the nitrate.

Although various colorimetric methods for nitrate are known,[2] the method presently proposed is based on a different mechanism of color development and has a higher sensitivity.

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[2] D. F. Boltz, "Colorimetric Determination of Nonmetals," Interscience Publisher, New York (1958), p. 135.