A New Method for the Determination of Nitrate Ions by Atomic Absorption Spectrophotometry

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In the course of our studies of the solvent extraction of anions with metal chelate cations,[1] it was found that a small amount of nitrate could be extracted into methyl isobutyl ketone (MIBK) when neo-cuproine* was contained in the organic phase and when copper(I) ions were present in the aqueous phase. This paper is concerned with the determination of nitrate ions by atomic absorption spectrophotometry. Figure 1 shows the absorption spectra in the organic phase. It may be observed that the presence of nitrate leads to a considerable increase in the extraction. The absorbance maximum of the extracted species is at 456 mμ. The chemical formula of the extracted species was determined to be [Cu(Neocup.*)$_2$NO$_3$]. It was also found that there is a linear relationship between the concentration of nitrate in the aqueous solution and the absorbance at 456 mμ of the organic phase. These facts suggest that it may be possible to determine the nitrate ions by spraying the extracted MIBK solution into the flame of an atomic absorption spectrophotometer using a copper hollow-cathode lamp (3247Å). The recommended procedure for the calibration curve is given below.

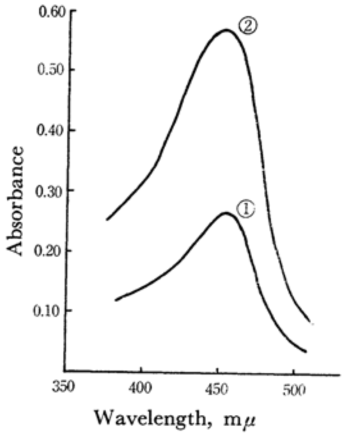

Fig. 1. Absorption spectra.

Water phase	Cu^{2+}	8×10^{-4} M
	Hydroxylamine	0.4%
	Phosphate	5×10^{-2} M
	NO_3^-	4×10^{-5} M
	pH	4.0

MIBK phase: Neo-cuproine 1×10^{-4} M
① Extracts by MIBK without nitrate ions
② Extracts by MIBK with nitrate ions
Reference: MIBK

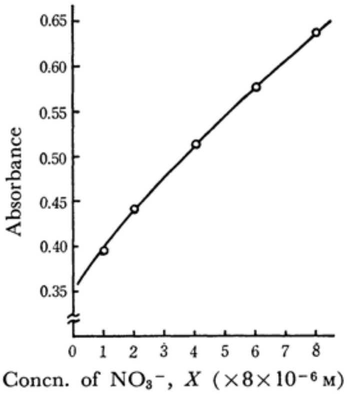

Fig. 2. Calibration curve (Reference: MIBK).

Two milliliters of the cupric sulfate solution (1×10^{-2} M), 2 ml. of the hydroxylamine sulfate solution (5%), 5 ml. of the buffer solution (0.25 M phosphate), and varying amounts of the standard nitrate solution (2×10^{-4} M, 1—8 ml.) were mixed. After the solution had been diluted with water to 25 ml., it was shaken for 2 min. with 10.0 ml. of a MIBK solution containing neo-cuproine (2×10^{-3} M). The atomic absorption measurements of the organic phase were made by using a Hitachi model 139—0420 atomic absorption spectrophotometer equipped with a copper hollow-cathode source. In atomic absorption spectrophotometry, it has generally been considered that the special spectral line issuing from the same metal as the element to be determined should be used. This has been a fairly great disadvantage in some cases because of the necessity of a special light source. Moreover, it has not been possible to apply the atomic absorption method to most non-metals. In this paper, we have suggested the possibility of determining some anions such as nitrate by solvent extraction with a metal chelate cation using a proper solvent and an appropriate hollow-cathode source.

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[1] Y. Yamamoto et al., This Bulletin, **37**, 434, 594, 785 (1964); **38**, 499, 1494 (1965).

* Neocup=neo-cuproine=2, 9-dimethyl-1, 10-phenanthroline.