

Determination of Iron in Aqueous Samples by UV-Vis Spectroscopy

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Introduction

An excellent and sensitive photometric method for the determination of iron is based upon the formation of the orange-red complex of ferrous iron with 1,10-phenanthroline (orthophenanthroline), or one of its derivatives. Ordinarily, the procedure is carried out under mildly acidic conditions to prevent precipitation of various iron salts (e.g. phosphates), but careful control of pH is not required. Since iron is the second most abundant metal on Earth, the chief difficulty in performing this analysis is not in finding the metal present, but in avoiding finding the metal that ought not to be present.

Reagents

Prepare accurately a working standard approximately 50 ppm in iron by dissolving ferrous ammonium sulfate in water, adding 1 mL concentrated sulfuric acid, then making up to 250 mL. Dissolve *ca.* 10 g hydroxylamine hydrochloride in 100 mL water (nominally 10% solution) and introduce enough sodium citrate to bring the pH to around 4.5. Take *ca.* 25 g sodium citrate and make up to 100mL of solution. Dissolve *ca.* 20 mg sodium bathophenanthroline disulfonate (i.e. 4,7-diphenyl-1,10-phenanthroline disulfonate) in 25 mL water by warming in a water bath to speed dissolution.

Procedure

Measure a 5.0 mL aliquot of the standard iron solution into a test tube and then, add sodium citrate solution dropwise from a pipet until a pH of around 4.5 is obtained. Noting the volume of sodium citrate required, discard this solution. Now measure a second 5.0 mL aliquot of the iron standard into a 100-mL volumetric flask. Add 1 mL of the hydroxylamine solution, 2.0 mL of the bathophenanthroline disulfonate solution and the previously determined amount of sodium citrate solution required to buffer at pH 4.5. Allow the mixture to stand for 5 minutes, then dilute to the mark with water. Measure the absorbance at 535 nm, or in a filter-based instrument fitted with a green filter, employing DI water as the blank.

Prepare at least three other standards so that a range of absorbances from about 0.1 to 1.0 will be covered and construct a calibration curve. Subsequently, the best fit to these data should be determined by a least squares regression analysis.

Obtain set aqueous iron solutions of unknown concentration from your instructor. Pipet a 5.0 mL aliquot of this into a test tube, then adjust the pH to around 4.5 by addition of sodium citrate solution, noting the quantity required. Discard this solution. Transfer a fresh 5.0-mL aliquot of the unknown to a 100-mL volumetric flask, add 1 mL of the hydroxylamine hydrochloride and 2.0 mL of the bathophenanthroline disulfonate solutions. Introduce the necessary amount of sodium citrate solution to achieve buffering at pH 4.5, allow the mixture to stand for 5 minutes, then dilute to the mark with water. Withdraw an aliquot of the solution and measure its absorbance. Determine the concentration of iron in the sample in ppm as it was supplied to you, reporting your result in terms of 95% confidence limits.

Questions

- (1) Draw the structure of bathophenanthroline disulfonate and describe the form of its Complex with ferrous iron.
- (2) What are the principle interferences in determinations of this kind?
- (3) How might you attempt to improve upon the sensitivity of the method?

References

H. Beinert, *Methods in Enzymology*, Vol. LIV, Academic Press (1978) pp. 435-445.

D. A. Skoog, D. M. West, and F. J. Holler, "Fundamentals of Analytical Chemistry," 6th Ed., Saunders College Publishing (1992) pp. 881-883.