The Spectrophotometric Determination of Nitrate Ion in 75% Sulfuric Acid[1]

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While investigating the color-forming reactions of 4,5-dihydroxynaphthalene-2,7-disulfonic acid (chromotropic acid) with various cations in concentrated sulfuric acid, it was observed that salts containing an ionizable nitrate group produced an intense yellow color.

Qualitative tests indicated that the color intensity varied with nitrate concentration. It was also observed that few other anions produced competing colors. Oxidizing agents such as bromates and iodates yielded the color of free bromine and iodine.

Therefore because of the promising nature of the colored species, and because of the need for a better colorimetric method for nitrate, the system of chromotropic acid, nitrate and sulfuric acid was investigated with reference to the possibility of devising a quantitative analytical procedure.

Experimental

A 0.01 M. nitrate solution was prepared by dissolving ammonium nitrate in 95% sulfuric acid. A 0.025 M solution of chromotropic acid was prepared by dissolving the sodium salt in 95% sulfuric acid. These solutions are instable when exposed to light and the reagent must either be stored in the dark or, preferably, made up before each analysis. All photometric data were obtained from the General Electric recording spectrophotometer using 1 cm. cells.

The Nitrate-Chromotropic Acid System

The spectrophotometric curve shows the presence of an absorbance maximum at 416μ. Solutions of ammonium nitrate, chromotropic acid and sulfuric acid were prepared differing only in the per cent of acid (by volume). No appreciable color develops when the solution is less than 50% sulfuric acid. From the standpoint of color intensity, it is apparent that any concentration of acid from 60% to 95% would be satisfactory, but the color stability (to be mentioned later) dictates use of approximately 75% sulfuric acid.

These investigations showed, further, that if the solutions are prepared by diluting 95% sulfuric acid with water, the heat generated seriously alters the shape of the absorption spectrum. Because of this, it is necessary to add the chromotropic acid reagent to the nitrate solution while simultaneously cooling it in a cold water bath. This removes the interference.

The absorbance decreases with increasing temperature of the solutions after color formation. Thus, for a five degree change in temperature

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the absorbance changes only 0.006 to 0.015 units, a maximum change of under 2%. Therefore, exact temperature control is not necessary since small fluctuations in temperature will not cause serious error in concentration measurements.

Color Stability

A series of solutions varying in nitrate concentrations, and containing 5 x 10^{-3}mμ. in chromotropic acid were prepared in 95% sulfuric acid. In addition to fading, the absorbance curve for any given concentration of nitrate was not reproducible. In 85% sulfuric acid, fading was again present though less pronounced.

A time study was made on two 2 x 10^{-4} M nitrate and 5 x 10^{-3} M chromotropic acid solutions in 75% sulfuric acid. Complete color development occurs within a few minutes after mixing. The system is then stable for a period of two hours following which it begins to fade slowly.

Precision Studies

The precision of the method was determined for concentrations at the middle and the extremes of the applicable concentration range. Six separately prepared samples were analyzed at each concentration. The average absorbance value, the standard deviation and the corresponding uncertainty in the estimation of the nitrate were determined. The standard deviation represents errors of $\pm$8% at 10^{-5} M nitrate to $\pm$0.5% at 4 x 10^{-4} M.

Interferences

The interference of various anions and cations was determined by measuring solutions in which the diverse ion concentration was one hundred times the nitrate concentration. The absorbance was then compared to a similar solution containing only the nitrate ion.

Under these conditions acetate, fluoride, perchlorate, magnesium and copper show no interference. Cyanate, phosphate, aluminate, zinc and calcium interfere but slightly. Thiocyanate and tetraborate almost completely destroy the color. Iron and chlorides interfere seriously. Nitrites produce the same color as nitrates. It seems likely that the nitrite is oxidized to nitrate and interferes simply by formation of additional color. Attempts to prevent this color formation by the addition of reducing agents, both before and after addition of the nitrite, were unsuccessful.

Chloride ion is known to be one of the chief interferences in colorimetric nitrate determinations. It was, therefore, studied in somewhat greater detail. The system was investigated using various amounts and ratios of nitrate ion, chloride ion, and chromotropic acid. The results demonstrated that a large excess of chloride cannot be tolerated and that the larger the nitrate concentration, the greater the effect of the chloride ion.

Summary

The method for the determination of nitrate using chromotropic acid in 75% sulfuric acid is applicable in the range of 0.1 to 7.0 parts per mil-

lion. The accuracy is observed to be about ±3%. The method compares favorably with other colorimetric methods for the determination of nitrate ion from the standpoint of sensitivity, convenience, reliability and interferences.

Literature Cited

1. SNELL, T. D., and SNELL, C. T. 1949. "Colorimetric Methods of Analysis," Vol. II, p. 792. D. Van Nostrand, New York.