Spectrophotometric Determination of Nitrate in Water

1. INTRODUCTION

Nitrate in water has been determined by the phenol-disulfonic acid method since 1863. Unfortunately, the method suffers from a number of interferences, the most significant being due to chlorides. The method lacks sensitivity and requires evaporation to dryness of relatively large samples of water. Ultraviolet spectrophotometry has been proposed (10.1) as an alternate method which is free from chloride interference. However, nitrite, chromium and organic matter do interfere unless compensated for through use of special correction curves. Reduction of nitrate to nitrite with subsequent measurement using a modified Griess reaction has been widely used. Although such methods are quite sensitive, a number of significant interferences detract from their appeal. Brucine produces an intense yellow with nitrate in the presence of acid. Chloride does not interfere and other constituents likely to be present in water have little or no effect (10.2). The method of choice for most applications is the chromotropic acid procedure (10.3) which is both sensitive and free from critical interferences. This latter method is accurate and the technique involved is straightforward.

2. SCOPE AND FIELD OF APPLICATIONS

This method is suitable for determining nitrate concentrations in natural waters and it can be applied directly to the analysis of water without recourse to evaporation or precipitation steps. No sample preparation is required unless suspended material is present; in which case the impurities can be removed by centrifugation or filtration. Reliable results can be obtained over the range 0.2-20mg/l of nitrate. Interferences due to substances such as nitrite, oxidizing agents, chloride and iron (III) which normally interfere in nitrate determinations have been eliminated.

3. PRINCIPLE

The method is based on the reaction of nitrate with chromotropic acid. The absorbance of the resulting yellow solution is proportional to the nitrate concentration. Potential interferences have been eliminated through the addition of excess sodium sulfite which removes interferences due to oxidizing agents, and addition of urea which eliminates nitrite interference. Reactions of chloride are masked by the addition of antimony (III).

4. REAGENTS

4.1 *Standard nitrate solution*

Dissolve 1.371g of reagent grade sodium nitrate in distilled water and dilute to one liter. This gives a nitrate concentration of 1mg/ml. A series of standards can be prepared by suitable dilutions.

4.2 *Sulfuric acid*

Use analytical reagent grade concentrated acid which is free from nitrate.

4.3 *Purified chromotropic acid*

Prepare a saturated solution of the disodium salt of 1,8-dihydroxy-3,6-naphthalene disulfonic acid. Process twice using decolorizing charcoal. Crystallize the reagent from the filtered solution by adding sulfuric acid. Filter, wash several times with ethanol and dry below 80°C. Prepare a 0.1% solution of the reagent in concentrated sulfuric acid. The reagent solution is colorless and is stable for two weeks.

4.4 *Sulfite – urea solution*

Dissolve 5g of urea and 4g of reagent grade anhydrous sodium sulfite and dilute to 100ml with distilled water.

4.5 *Antimony solution*

Heat 0.5g of antimony metal in 80ml of concentrated sulfuric acid until all the metal is dissolved. Cool the solution and add to 20ml of ice water. When kept overnight, if any salt crystallizes, redissolve by heating.

5. APPARATUS

Spectrophotometer suitable for measurement of absorbance at 410nm and equipped with matched quartz cells.

6. SAMPLING

Any acceptable procedure for obtaining representative samples from natural waters may be used. The samples to be analyzed are transferred by pipet to volumetric flasks and are treated according to Section 7, Procedure.

7. PROCEDURE

Pipet 2.5ml of sample into dry 10ml volumetric flasks. To each flask add 1 drop of sulfite-urea solution; place the flasks in a tray of cold water (10-20°C) and add 2ml of the antimony sulfate solution. Swirl the flasks during the addition of each solution. After the mixtures have stood in the bath for about 4 minutes, add 1ml of chromotropic acid reagent; swirl the flasks again and allow them to stand in the cooling bath for an additional 3 minutes. Add concentrated sulfuric acid to adjust the volume to the 10ml mark; stopper the flasks and invert 4 times in order to ensure adequate mixing. Finally, allow the solutions to stand for 4-5 minutes at room temperature and again adjust the volume to the 10ml mark with concentrated sulfuric acid. Mix carefully in order not to introduce gas bubbles. After waiting at least 15 minutes, read the absorbance at 410nm. For running blank experiments, substitute double-distilled water for sample or nitrate solutions.

8. CALIBRATION CURVE

By diluting the standard solution, prepare a series of standards containing 0.1, 0.4, 0.7, 1.0, 2.0, 4.0 and 8.0mg/l of nitrate. Carry out the instructions in Section 7, Procedure. Plot absorbance versus nitrate concentration; a linear plot should be obtained.

9. REPRODUCIBILITY

The method is a reliable one. At the 1mg/l level for nitrate the coefficient of variation at the 95% confidence limit is 4%.

10. REFERENCES

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10.3 West, P. W. and Ramachandran, T. P. *Anal. Chim. Acta*, **35**, 317, 1966.