METHOD 9200

NITRATE

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of ground water, drinking, surface, and saline waters, and domestic and industrial wastes. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.

1.2 The applicable range of concentration is 0.1 to 2 mg NO_3-N per liter of sample.

2.0 SUMMARY OF METHOD

2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H_2SO_4 solution at a temperature of 100°C. The color of the resulting complex is measured at 410 nm. Temperature control of the color reaction is extremely critical.

3.0 INTERFERENCES

3.1 Dissolved organic matter will cause an off color in 13 N H_2SO_4 and must be compensated for by additions of all reagents except the brucine- sulfanilic acid reagent. This also applies to natural color, not due to dissolved organics, that is present.

3.2 If the sample is colored or if the conditions of the test cause extraneous coloration, this interference should be corrected by running a concurrent sample under the same conditions but in the absence of the brucine-sulfanilic acid reagent.

3.3 Strong oxidizing or reducing agents cause interference. The presence of oxidizing agents may be determined by a residual chlorine test; reducing agents may be detected with potassium permanganate.

3.3.1 Oxidizing agents' interference is eliminated by the addition of sodium arsenite.

3.3.2 Reducing agents may be oxidized by addition of H_2O_2.

3.4 Ferrous and ferric iron and quadrivalent manganese give slight positive interferences, but in concentrations less than 1 mg/L these are negligible.

3.5 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for absolute control of temperature during the critical color development period cannot be too strongly emphasized.

4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer or filter photometer suitable for measuring absorbance at 410 nm.

4.2 Sufficient number of 40- to 50-mL glass sample tubes for reagent blanks, standards, and samples.

4.3 Neoprene-coated wire racks to hold sample tubes.

4.4 Water bath suitable for use at 100°C. This bath should contain a stirring mechanism so that all tubes are at the same temperature and should be of sufficient capacity to accept the required number of tubes without a significant drop in temperature when the tubes are immersed.

4.5 Water bath suitable for use at 10-15°C.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sodium chloride solution (30%): Dissolve 300 g NaCl in Type II water and dilute to 1 liter.

5.3 Sulfuric acid solution: Carefully add 500 mL concentrated H_2SO_4 to 125 mL Type II water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

5.4 Brucine-sulfanilic acid reagent: Dissolve 1 g brucine sulfate -- $(C_{23}H_{26}N_2O_4)_2 \cdot H_2SO_4 \cdot 7H_2O$ -- and 0.1 g sulfanilic acid ($NH_2C_6H_4SO_3H \cdot H_2O$) in 70 mL hot Type II water. Add 3 mL concentrated HCl, cool, mix, and dilute to 100 mL with Type II water. Store in a dark bottle at 5°C. This solution is stable for several months; the pink color that develops slowly does not affect its usefulness. Mark bottle with warning, **"CAUTION: Brucine Sulfate is toxic; do not ingest."**

5.5 Potassium nitrate stock solution (1.0 mL = 0.1 mg NO_3-N): Dissolve 0.7218 g anhydrous potassium nitrate (KNO_3) in Type II water and dilute to 1 liter in a volumetric flask. Preserve with 2 mL chloroform per liter. This solution is stable for at least 6 mon.

5.6 Potassium nitrate standard solution (1.0 mL = 0.001 mg NO_3-N): Dilute 10.0 mL of the stock solution (5.5) to 1 liter in a volumetric flask. This standard solution should be prepared fresh weekly.

5.7 Acetic acid (1+3): Dilute 1 volume glacial acetic acid (CH_3COOH) with 3 volumes of Type II water.

5.8 Sodium hydroxide (1 N): Dissolve 40 g of NaOH in Type II water. Cool and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Analysis should be done as soon as possible. If analysis can be done within 24 hr, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hr, they should be preserved with sulfuric acid (2 mL/L concentrated H_2SO_4) and refrigerated.

7.0 PROCEDURE

7.1 Adjust the pH of the samples to approximately 7 with acetic acid (Paragraph 5.7) or sodium hydroxide (Paragraph 5.8). If necessary, filter to remove turbidity. Sulfuric acid can be used in place of acetic acid, if preferred.

7.2 Set up the required number of sample tubes in the rack to handle reagent blank, standards, and samples. Space tubes evenly throughout the rack to allow for even flow of bath water between the tubes. This should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, run a set of duplicate samples to which all reagents, except the brucine-sulfanilic acid, have been added.

7.3.1 Add 0.5 mL brucine-sulfanilic acid reagent (Paragraph 5.4) to each tube (except the interference control tubes) and carefully mix by swirling; then place the rack of tubes in the 100°C water bath for exactly 25 min.

CAUTION: Immersion of the tube rack into the bath should not decrease the temperature of the bath by more than 1-2°C. In order to keep this temperature decrease to an absolute minimum, flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack. If color development in the standards reveals discrepancies in the procedure, the operator should repeat the procedure after reviewing the temperature control steps.

7.4 Pipet 10.0 mL of standards and samples or an aliquot of the samples diluted to 10.0 mL into the sample tubes.

7.5 If the samples are saline, add 2 mL of the 30% sodium chloride solution (Paragraph 5.2) to the reagent blank, standards, and samples. For freshwater samples, sodium chloride solution may be omitted. Mix contents of tubes by swirling and place rack in cold-water bath (0-10°C).

7.6 Pipet 10.0 mL of sulfuric acid solution (Paragraph 5.3) into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.7 Remove rack of tubes from the hot-water bath, immerse in the cold-water bath, and allow to reach thermal equilibrium (20-25°C).

7.8 Read absorbance against the reagent blank at 410 nm using a 1-cm or longer cell.

7.9 Calculation:

7.9.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against mg/L NO_3-N. (The color reaction does not always follow Beer's law.)

7.9.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and determine mg/L NO_3-N. Multiply by an appropriate dilution factor if less than 10 mL of sample is taken.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Linear calibration curves must be composed of a minimum of a blank and five standards. A set of standards must be included with each batch of samples.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Twenty-seven analysts in fifteen laboratories analyzed natural-water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrogen, Nitrate (mg/L N)	Precision as Standard Deviation (mg/L N)	Accuracy as Bias (%)	Accuracy as Bias (mg/L N)
0.16	0.092	-6.79	-0.01
0.19	0.083	+8.30	+0.02
1.08	0.245	+4.12	+0.04
1.24	0.214	+2.82	+0.04

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D992-71, p. 363 (1976).

2. Jenkins, D. and L. Medsken, "A Brucine Method for the Determination of Nitrate in Ocean, Estuarine, and Fresh Water," Anal.Chem., 36, p. 610 (1964).

3. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 427, Method 419D (1975).

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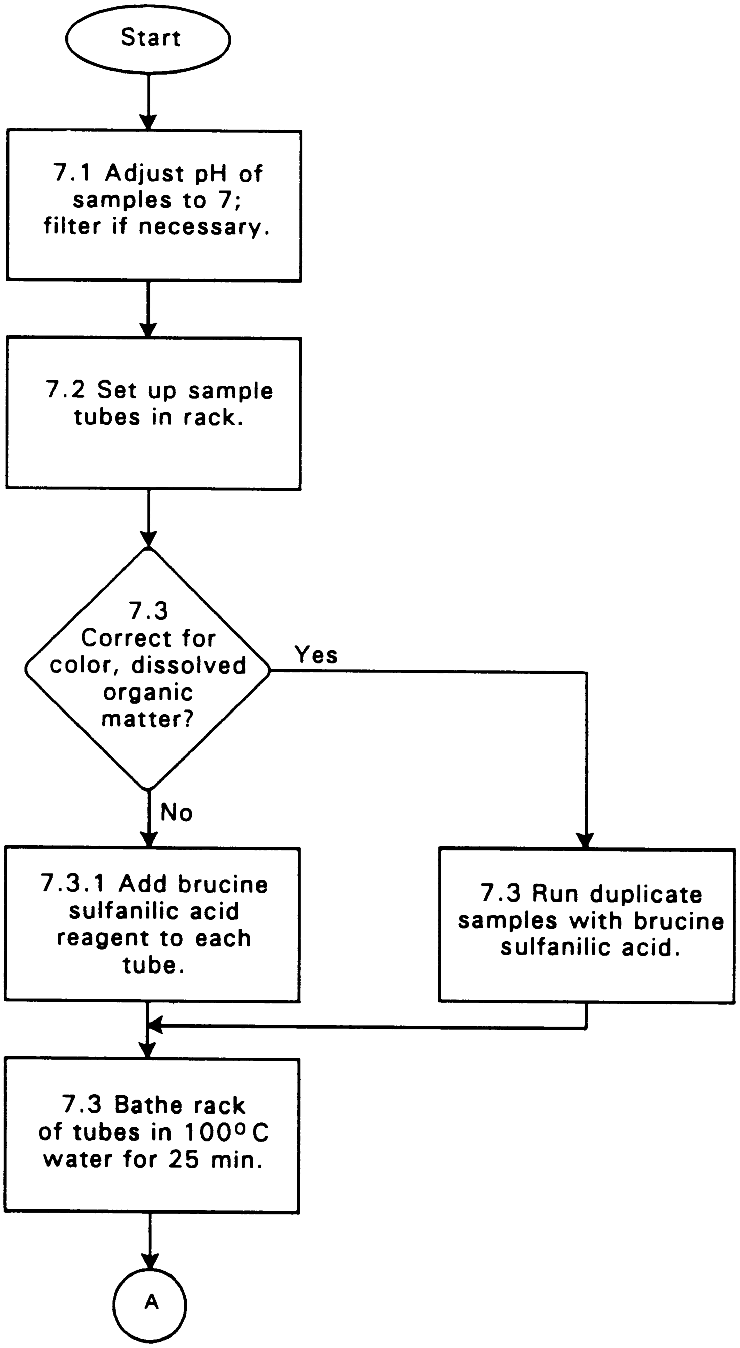

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