METHOD 9216

POTENTIOMETRIC DETERMINATION OF NITRITE
IN AQUEOUS SAMPLES WITH ION-SELECTIVE ELECTRODE

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0   SCOPE AND APPLICATION

1.1   This method can be used for measuring nitrite in drinking water, wastewater, and reagent waters. If this method is used for other types of water samples (i.e., surface water, ground water, etc.), method precision and accuracy must be demonstrated for each matrix type.

1.2   Ion selective electrodes (ISEs) must be used carefully and results must be interpreted cautiously, since an ISE may be affected by numerous analytical interferences which may either increase or decrease the apparent analyte concentration, or which may damage the ISE. Effects of most interferences can be minimized or eliminated by adding appropriate chemical reagents to the sample. Obtaining the most accurate results, therefore, requires some knowledge of the sample composition.

NOTE: ISE manufacturers usually include a list of interferences in the instruction manual accompanying an ISE, along with recommended methods for minimizing or eliminating effects of these interferences.

1.3   Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.4   Use of this method is restricted to use by, or under supervision of, personnel trained and knowledgeable in the operation of an ISE. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0   SUMMARY OF METHOD

This method uses a nitrite-selective electrode. All standards and samples are mixed with an equal volume of nitrite interference suppressor solution (NISS). A calibration curve is constructed by recording the nitrite calibration standard readings using an appropriate meter or by manual plotting. Samples are then read in the same manner, and the concentrations reported by the meter or read from the graph.

3.0   DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0   INTERFERENCES

4.1   Some anions, if present at high enough levels, are electrode interferences and will cause measurement errors. Table 1 displays the levels of possible interferences causing a 10% error. NISS is mixed in an equal volume with standards as well as with samples. For example, 25 mL of sample would be mixed with 25 mL of NISS. This procedure ensures that samples and standards are properly buffered, have a similar background and that no correction factor is needed for the dilution. Figure 1 shows how the nitrite electrode response changes with pH. This is compensated for by the addition of the NISS. Selectivity is mathematically demonstrated by the following equation:

$$E = E^{'} + s \log[c_j + 3 K_{ij} \, c_j^{Zj}]$$

Where:

$E^{'}$ = Reference potential

s = Slope

c_j = Primary ion concentration

K_{ij} = Selectivity Coefficient

c_j^{Zj} = Interfering ion concentration

Zj = charge ratio of interfering ion

Successful analytical conditions depend upon:

$$c_j \gg 3 K_{ij} \, c_j^{Zj}$$

4.2   Temperature changes affect electrode potentials. Therefore, standards and samples must be equilibrated at the same constant temperature ($\pm 1 \, \mathrm{E}$C).

4.3   The user should be aware of the potential for interferences from colloidal substances and that, if necessary, the samples should be filtered. If the samples are filtered, the associated method blanks must also be filtered.

4.4   Standard electrode filling solutions containing high levels of KCl should not be used as the reference electrode filling solution.

4.5   If electrodes are exposed to samples with nitrite concentrations greater than 20 mg/L, their response may become very sluggish when again measuring at a lower concentration. If this occurs, soak the electrodes for 8 - 12 hr in a mixture of the 0.5 mg/L standard and NISS.

4.6   ISE manufacturers usually include a list of interferences in the instruction manual accompanying an ISE, along with recommended methods for minimizing or eliminating effects of these interferences.

5.0   SAFETY

5.1   This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2   WARNING: Use a hood to avoid exposure to toxic gases released during acidification.

5.3   It is the responsibility of the user to prepare, handle, and dispose of electrolyte solutions in accordance with all applicable Federal, state, and local regulations.

6.0   EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1   A pH/mV meter -- Capable of reading to 0.1 mV or an ISE meter.

6.2   Nitrite ISE (Orion 93-46 or equivalent) and double-junction reference electrode (Orion 90-01 or equivalent).

6.3   Thermally isolated magnetic stirrer, polytetrafluoroethylene (PTFE)-coated magnetic stir bar, and stopwatch.

6.4   Volumetric flasks -- Class A, 100 mL and 1 L.

6.5   Volumetric pipets -- Class A, 5 mL, 10 mL and 50 mL.

7.0 REAGENTS AND STANDARDS

7.1   Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2   Reagent water -- Reagent water must be interference free. All references to water in this method refer to reagent water, unless otherwise indicated.

7.3   Ionic strength adjuster (ISA) solution (2M), $(NH_4)_2SO_4$ -- Dissolve 26.4 g of ammonium sulfate in reagent water to make 100 mL of solution.

7.4   Nitrite reference electrode filling solution (Orion 900046 or equivalent).

7.5   Nitrite interference suppressor solution (NISS) (Orion 934610 or equivalent).

7.6   1000 mg/L nitrite as N, stock standard -- Weigh out 4.93 g of ACS reagent grade sodium nitrite that has been dried for 24 hr in a desiccator. Place in a clean 1-L volumetric flask. Add approximately 200 mL of reagent water and mix to dissolve. Add two drops of NaOH and make to volume. Mix by inverting 20 times.

7.7   100 mg/L nitrite as N, standard -- Pipet 10.0 mL of the 1000 mg/L stock standard into a clean 100-mL volumetric flask. Bring to volume and mix well. Replace this standard monthly.

7.8   10 mg/L nitrite as N, standard -- Pipet 10.0 mL of the 100 mg/L standard into a clean 100-mL volumetric flask. Bring to volume and mix well. Replace this standard weekly.

7.9   5 mg/L nitrite as N, standard -- Pipet 50.0 mL of the 10 mg/L standard solution into a clean 100-mL volumetric flask. Bring to volume with reagent water and mix well. This standard should be replaced daily.

7.10   1 mg/L nitrite as N, standard -- Pipet 10.0 mL of the 10.0 mg/L standard into a clean 100-mL volumetric flask. Bring to volume with reagent water and mix well. This standard should be replaced daily.

7.11   0.5 mg/L nitrite as N, standard -- Pipet 5.00 mL of the 10.0 mg/L standard into a clean 100-mL volumetric flask. Bring to volume with reagent water and mix well. This standard should be replaced daily.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1   See the introductory material to Chapter Three, "Inorganic Analytes."

8.2   Samples should be stored at #6 ΕC and should be analyzed within 48 hr of collection.

9.0   QUALITY CONTROL

9.1   Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2   Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency by following the test procedure described in this method and generating data of acceptable accuracy and precision for the target analyte in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff are trained or significant changes in instrumentation are made.

9.3   Initial calibration verification standard (ICV)

After performing the calibration step (Sec. 10.0), verify calibration by analyzing an ICV. The ICV contains a known nitrite concentration at the mid-range of the calibration standards and must be from an independent source. ICV recovery should be 90 - 110 percent. If not, the source of error should be found and corrected. An acceptable ICV must be analyzed prior to sample analysis. The ICV also serves as a laboratory control sample.

9.4   Continuing calibration verification standard (CCV)

A CCV must be analyzed after every 10 samples and after the final sample. The CCV contains a known nitrite concentration at the mid-range of the calibration standards and is made from the same source as the calibration curve. The CCV recovery should be 90 - 110 percent. If not, the error source should be found and corrected. If ISE calibration has changed, then all samples analyzed since the last acceptable CCV must be reanalyzed.

9.5   Reagent blank

A reagent blank must be analyzed after the ICV and after every CCV. A reagent blank consists of 25.0 mL of reagent water with 25.0 mL of NISS added. The indicated reagent blank concentration should be less than 1 mg/L of nitrite. If not, then the contamination source should be found and corrected. All samples analyzed since the last acceptable reagent blank must reanalyzed.

9.6   Matrix spike/matrix spike duplicate (MS/MSD)

For each batch of samples processed, at least one MS/MSD pair should be carried through the entire sample preparation and analytical process. The MS/MSD are intra-laboratory split samples, spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. MS/MSD samples should be spiked at the project-specific action level or, when lacking project-specific action levels, between the low- and mid-level standards.

Acceptance criteria should be set at a laboratory-derived limit developed through the use of historical analyses. In the absence of historical data, this accuracy limit should be set at ± 20% of the spiked value and the precision limit should be set at # 20 relative percent difference (RPD). Acceptance limits derived from historical data should be no wider that ± 20%. Refer to Chapter One for guidance. If the bias and precision indicators are outside the laboratory control limits or if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, an interference should be suspected (refer to Sec. 4.0).

10.0 CALIBRATION AND STANDARDIZATION

10.1   When using a nitrate ISE and a separate double-junction reference electrode, ensure that reference electrode inner and outer chambers are filled with solutions recommended by the manufacturer. Equilibrate the electrodes for at least 1 hr in a 100 mg/L nitrite standard before use.

10.2   Calibrate the nitrite ISE using standards that narrowly bracket the expected sample concentration. If the sample concentration is unknown, calibrate with 0.5 mg/L, 1.0 mg/L, and 5.0 mg/L nitrite standards.

10.3   Add 25.0 mL of a standard solution and 25.0 mL of the NISS into a 100 mL beaker to make each calibration standard. Add a PTFE-coated magnetic stir bar, place the beaker on a magnetic stir plate, and stir at slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. If using an ISE meter, calibrate the meter in terms of nitrite concentration following the manufacturer's instructions. If using a pH/mV meter, record the meter reading (mV) as soon as the reading is stable, but in no case should the time exceed 5 min after immersing the electrode tips.

10.4   Prepare a calibration curve by plotting measured potential (mV) as a function of the logarithm of nitrite concentration. The slope must be 54 - 60 mV per decade of nitrate concentration. If the slope is not acceptable, the ISE may not be working properly. For corrective action, consult the ISE operating manual.

11.0 PROCEDURE

11.1   Allow samples and standards to equilibrate to room temperature.

11.2   Prior to and between analyses, rinse the electrodes thoroughly with reagent water and gently shake off excess water. Low-level measurements are faster if the electrode tips are first immersed 5 min in reagent water.

11.3   Add 25.0 mL of sample and 25.0 mL of NISS to a 100-mL beaker. Add a PTFE-coated magnetic stir bar. Place the beaker on a magnetic stir plate and stir at a slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. Record the meter reading (mV or concentration) as soon as the reading is stable, but in no case should the time exceed 5 min after immersing the electrode tips. If reading mV, determine nitrite-nitrogen concentration from the calibration curve.

11.4   When analyses have been completed, rinse the electrodes thoroughly with water and store them in a 100 mg/L nitrate standard solution. If the electrodes will not be used again for more than one day, drain the reference electrode internal filling solutions, rinse with reagent water, and store dry or store according to the manufacturer's instructions.

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.3 for information on data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1   Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods.   Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2   Figure 2 is an example of a calibration curve for nitrite at 0.5 mg/L, 1 mg/L, and 5 mg/L. Figure 3 displays an example of a low level calibration curve for nitrite at 0.05 mg/L, 0.1 mg/L, 0.2 mg/L, and 0.5 mg/L. These data are provided for guidance purposes only.

13.3   Table 1 displays the levels at which known interferences may impact the analysis. These data are provided for guidance purposes only. Refer to Sec. 4.0 for a discussion on interferences.

14.0 POLLUTION PREVENTION

14.1   Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2   For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Applications Laboratory Report, "Tests in Water Samples by Nitrite Electrode and 'Standard Methods' Colorimetric Analysis," ATI Orion, Boston MA, April 1995.

2. Model 93-46 Nitrite Electrode Instruction Manual, ATI Orion, Boston MA, 1994.

3. S. J. West, X. Wen, M. S. Frant, N. A. Chaniotakis, "Determination of Nitrite in Foods and Wastewater Using a Nitrite-Selective Electrode," Pittsburgh Conference, March 1994.

4. S. J. West, X. Wen, "Determination of Nitrate, Nitrite, and Ammonia in Advanced Secondary Effluent by Means of Ion-Selective Electrodes," Pittsburgh Conference, March 1994.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the table and figures referenced by this method. A flow diagram of the procedure follows the table and figures.

TABLE 1

EXAMPLE NITRITE ELECTRODE SELECTIVITY DATA

Interfering Ion	log K_{ij}	10% Error Ratio (ppm)
Hydroxide	2.8	-
Fluoride	-3.1	170
Chloride	-3.1	320
Chlorate	-3.4	1600
Perchlorate	-3.1	830
Bromide	-3.0	570
Iodide	-1.2	15
Sulfate	-4.1	1100
Nitrate (N)	-3.3	200
Phosphate	-4.0	9500
Polyphosphate	-4.4	3400
Bicarbonate	-3.3	870
Acetate	-3.2	720
Lactate	-4.9	Very high
Phthalate	-2.5	380
Ascorbate	-4.2	Very high
Salicylate	-0.8	7.0

Data taken from Reference 1.

FIGURE 1

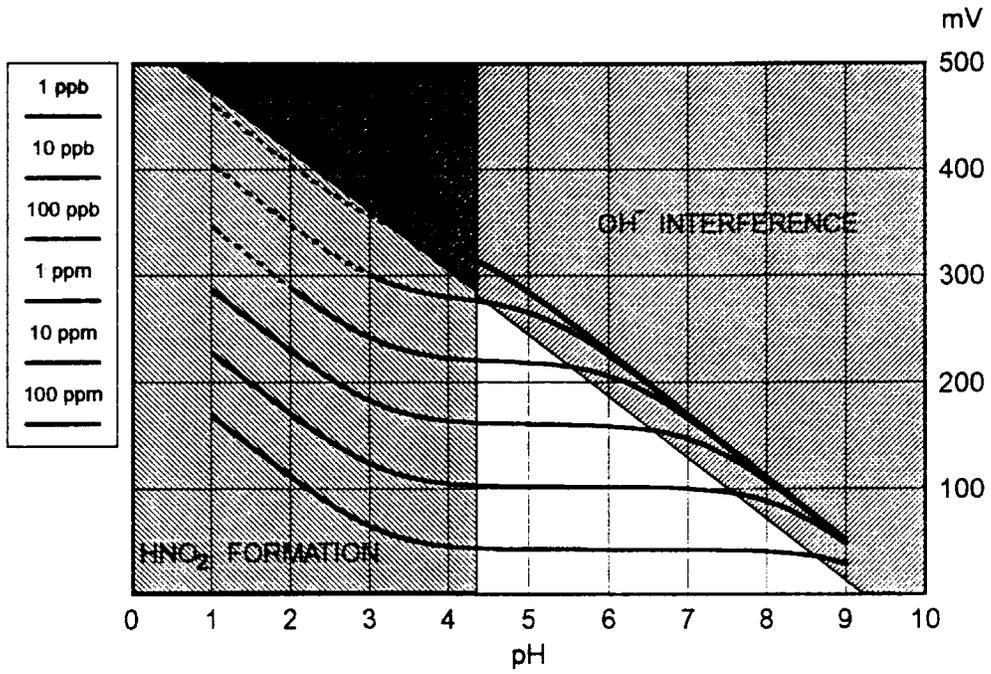## EXAMPLE NITRITE ELECTRODE pH RESPONSE

FIGURE 2

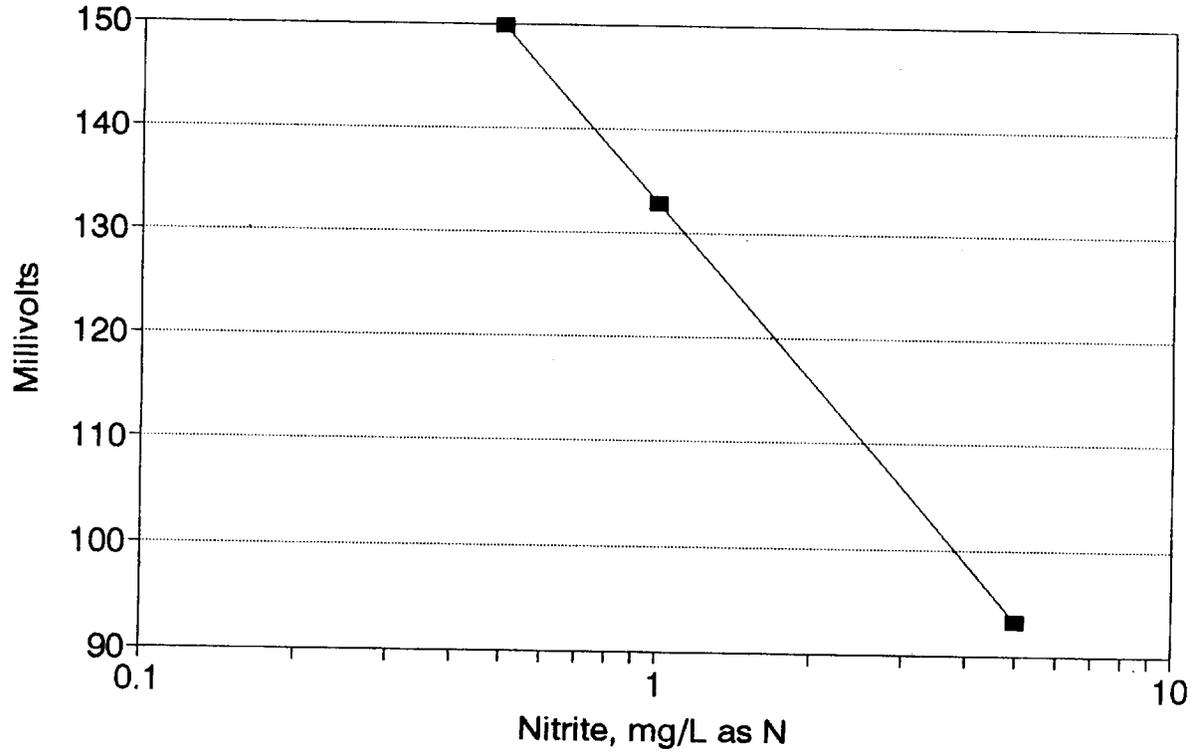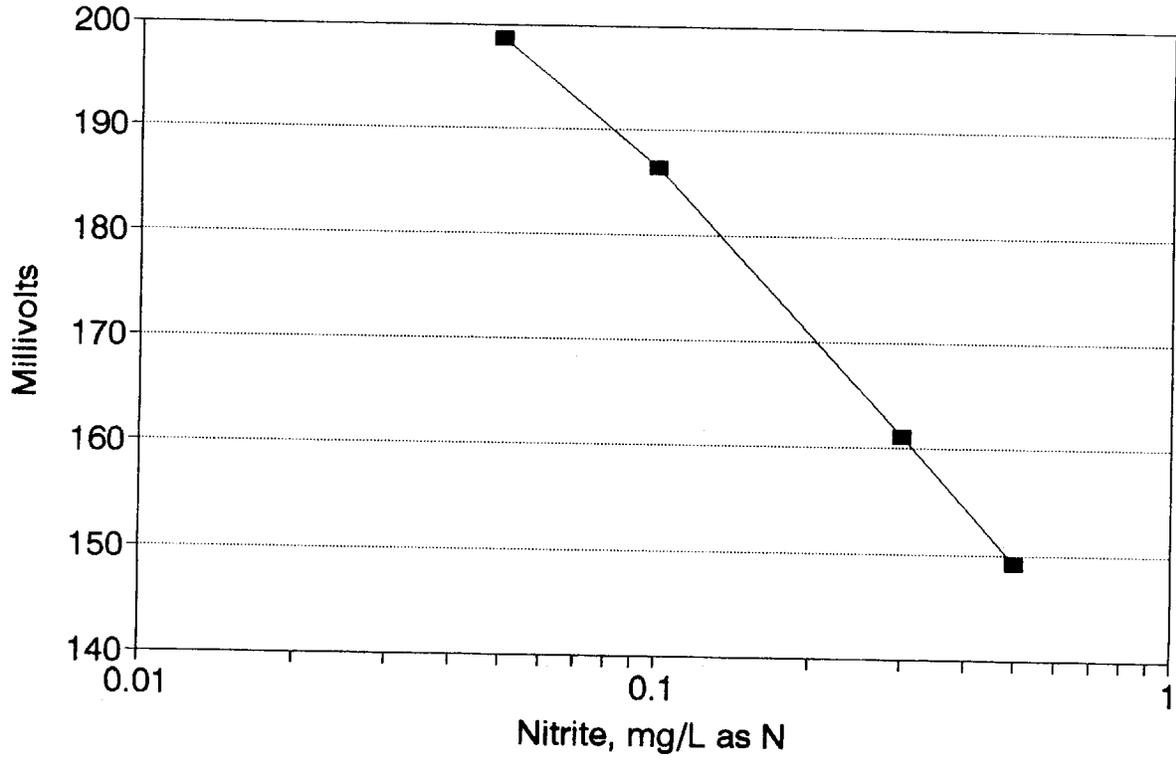EXAMPLE CALIBRATION CURVE FOR STANDARD LEVEL OF NITRITE

FIGURE 3

EXAMPLE CALIBRATION CURVE FOR LOW LEVEL NITRITE METHOD

METHOD 9216

POTENTIOMETRIC DETERMINATION OF NITRITE
IN AQUEOUS SAMPLES WITH ION-SELECTIVE ELECTRODE

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                    ┌─────────┐
                    │  Start  │
                    └─────────┘
                         │
                         ▼
          ┌─────────────────────────────┐
          │        10.1 - 10.2          │
          │         Calibrate           │
          │        Nitrite ISE.         │
          └─────────────────────────────┘
                         │
                         ▼
          ┌─────────────────────────────┐
          │    11.1 Allow Standards     │
          │      and samples to         │
          │       equilibrate to        │
          │      room temperature.      │
          └─────────────────────────────┘
                         │
                         ▼
          ┌─────────────────────────────┐
          │    11.2 Rinse electrode     │
          │     with reagent water.     │
          └─────────────────────────────┘
                         │
                         ▼
          ┌─────────────────────────────┐
          │   11.3 Add 25 mL sample     │
          │   and 25 mL NISS to beaker, │
          │  and measure concentration  │
          │      using electrode meter  │
          │  and calculate concentration.│
          └─────────────────────────────┘
                         │
                         ▼
          ┌─────────────────────────────┐
          │   11.4 Drain reference      │
          │    electrode and clean.     │
          └─────────────────────────────┘
                         │
                         ▼
                    ┌─────────┐
                    │  Stop   │
                    └─────────┘
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