METHOD 9210A

POTENTIOMETRIC DETERMINATION OF NITRATE IN AQUEOUS SAMPLES WITH AN 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 may be used for measuring solubilized nitrate in drinking water, natural surface water, groundwater, domestic and industrial wastewater, soil extracts (ASTM Standards D 4646, D 5233 or D 3987) and aqueous extracts of other solids.

NOTE: This method is for the analysis of the simple (non-complexed) nitrate ion rather than the total nitrate, because the analysis using the ion-selective electrode is not preceded by a distillation step.

1.2 A linear calibration (± 20% RSD) can be obtained over the range of 5.0 to 200 (mg/L). Results less than 5.0 mg/L will be biased high while results greater than 200 mg/L will be biased low.

1.3 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 (see Sec. 4.1). 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.

1.4 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.

1.5 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

2.1 Solubilized nitrate is determined potentiometrically using a nitrate ion-selective electrode (ISE) in conjunction with a double-junction reference electrode and a pH meter equipped with an expanded millivolt scale (mV), or an ISE meter capable of being calibrated directly in terms of nitrate concentration.

2.2 Standards and samples are mixed with an ionic strength adjustment solution. Calibration is performed by analyzing a series of standards and plotting mV vs. nitrate-nitrogen concentration on semilog paper, or by calibrating the ion meter directly in terms of nitrate concentration.

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 The nitrate electrode responds to numerous interfering anions. Most of the interferants, however, can be rendered harmless by adding suitable reagents. Cyanide, bisulfide, bicarbonate, carbonate, and phosphate are removed by adjusting the solution to pH 4 with boric acid. Chloride, bromide, and iodide are removed by adding silver sulfate solution. Nitrite is also an interferent, as shown in Table 1, and can be removed by adding sulfamic acid. The amounts of silver sulfate and sulfamic acid needed will vary based on the concentrations of interferants. As a general guide, 1 mL of silver sulfate will eliminate chloride interference in a 50-mL sample containing 35 mg/L of Cl^-. 1 mL of sulfamic acid solution will eliminate nitrite interference in a 50-mL sample containing 95 mg/L of NO_2^-.

4.2 Temperature changes affect electrode potentials (Reference 2). Therefore, standards and samples must be equilibrated at the same temperature (± 1 °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 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 pH/mV meter -- Capable of reading to 0.1 mV, may be automated.

6.2 Nitrate ISE and double-junction reference electrode.

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

6.4 Volumetric flask -- Class A, 100-mL.

6.5 Analytical balance -- Capable of accuracy to 0.001g.

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 specified.

7.3 Ionic strength adjustor (ISA) solution (2M), $(NH_4)_2SO_4$ -- Dissolve 26.4 g of ammonium sulfate in a 100-mL Class A volumetric flask and make to volume with reagent water.

7.4 Boric acid (1M), H_3BO_3, solution -- Dissolve 6.2 g of boric acid in a 100-mL Class A volumetric flask and make to volume with reagent water. This is the preservative solution for numerous anions and bacteria.

7.5 Silver sulfate (0.05M), Ag_2SO_4, solution -- Used to remove interferences, as noted in Sec. 4.1. Dissolve 1.6 g of silver sulfate in a 100-mL volumetric flask and make to volume with reagent water. A saturated silver sulfate solution contains approximately 5.5 g/L of solubilized silver.

7.6 Sulfamic acid (0.1M), $HOSO_2NH_2$, solution -- Used to remove nitrite from sample, as noted in Sec. 4.1. Dissolve 0.97 g of sulfamic acid in a 100-mL volumetric flask and make to volume with reagent water.

7.7 Nitrate calibration stock solution (1,000 mg/L), NO_3^--N -- Dissolve 7.218 g of potassium nitrate (dried for two hrs at 110 °C and stored in a desiccator) in reagent water and dilute to 1 L in a volumetric flask. Store in a clean bottle. This standard may also be purchased from a vendor.

7.8 Nitrate calibration standards -- Prepare a series of calibration standards by diluting the 1,000 mg/L nitrate standard. A suitable series is given in the table below. These standards should be replaced daily.

Volume of 1,000 mg/L NO_3^- Solution (mL)	Concentration when Diluted to 50.0 mL (mg/L NO_3^--N)
0.0500	1.00
0.150	3.00
0.500	10.0
1.50	30.0
5.00	100.0

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 In most environmental samples, nitrate is not affected by complexation, precipitation, inorganic oxidation-reduction reactions, and protonation. However, in the presence of a reducing agent (*e.g.*, organic matter), bacteria will utilize nitrate as an oxidant, causing a slow decrease in the nitrate concentration. This potential interference can be obviated by using a preservative. Therefore, samples must be preserved by adding 1 mL of 1M boric acid solution per 100 mL of sample at the time of sampling.

8.2 Samples should be stored at ≤6 °C and should be analyzed within 48 hr of collection.

8.3 Also see the introductory material to Chapter Three, "Inorganic Analytes."

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for 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. 10.1), verify calibration by analyzing an ICV. The ICV contains a known nitrate 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 nitrate 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.

9.4 Method blank

A method blank must be analyzed after the ICV and after every CCV. A method blank is a 1% solution of preservative solution in reagent water, mixed 50:1 with the ISA. The result for the method blank should be <1 mg/L nitrate. If not, then the contamination source should be found and corrected. All samples analyzed since the last acceptable method blank must be reanalyzed. If the samples are filtered, then the method blanks must also be filtered.

9.5 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 one hr in a 100 mg/L nitrate standard before use.

10.2 Calibrate the nitrate ISE using standards that narrowly bracket the expected sample concentration. If the sample concentration is unknown, calibrate with 3.00 mg/L and 30.0 mg/L nitrate standards.

10.3 Add 50.0 mL of standard, 0.50 mL of preservative solution, and 1.00 mL of ISA to a 100-mL beaker. 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 nitrate concentration by 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 five min after immersing the electrode tips.

10.4 Prepare a calibration curve by plotting measured potential (mV) as a function of the logarithm of nitrate 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 for 5 min in reagent water.

11.3 Add 50.0 mL of sample and 1.00 mL of ISA 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 nitrate-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 In a single-laboratory evaluation, a series of standards with known nitrate concentrations was analyzed with a nitrate ISE. Measurements were obtained over three consecutive days using an Orion 9307 nitrate ISE and an Orion 9002 double-junction reference electrode connected to an Orion 940 ISE meter. A two-point calibration (5.00 and 50.0 mg/L nitrate) was performed prior to analysis. The results are listed in Table 2. These data are provided for guidance purposes only.

13.3 In the same study as that mentioned in Sec. 13.2, three groundwater samples were spiked with nitrate at four different concentrations and measured with the nitrate ISE. The groundwater samples initially contained <0.1 to 2.3 mg/L of nitrate. Each spiked sample was analyzed at each concentration, and the mean recoveries and RSDs are given in Table 3. These data are provided for guidance purposes only.

13.4 A 50-g portion of soil, which initially contained 0.7 mg/kg of nitrate, was spiked with 25.0 mg/kg of nitrate to obtain an anion concentration in a single extract volume within the linear range of the ISE. The extract was then analyzed for nitrate using this ISE method, and 89% of the soil spike was recovered (Reference 3). These data are provided for guidance purposes only.

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. Model 93-07 Nitrate Electrode Instruction Manual. Orion Research, Inc., Boston, MA, 1986.

2. E. L. Miller, D. W. Waltman, and D. C. Hillman, "Single-Laboratory Evaluation of Fluoride, Chloride, Bromide, Cyanide, and Nitrate Ion-Selective Electrodes for Use in SW-846 Methods," Lockheed Engineering and Sciences Company for Environmental Monitoring Systems Laboratory, U.S. EPA, EPA/600/X-90/221, September 1990.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

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

TABLE 1

NITRATE ISE INTERFERENCES

Interference	Conc. (mg/L)	Measured Nitrate Conc. (mg/L)	RSD (%)
None	25.0	26	6.2
0.01 *M* H_2SO_4	25.0	24.5	5.9
100 mg/L NO_2^-	25.0	46	9.1
100 mg/L NO_2^- + 500 mg/L $HOSO_2NH_2$	25.0	26	6.3

Data taken from Reference 1.
These data are provided for guidance purposes only.

TABLE 2

EXAMPLE RESULTS FROM A SINGLE-LABORATORY ACCURACY EVALUATION OF A NITRATE ISE

Nitrate Conc. (mg/L)	Nitrate Detected (mg/L)	Recovery (%)	RSD (%)
0.100	1.01	1010	53
0.200	1.04	520	17
0.500	1.23	246	8
1.00	1.71	171	2
2.00	2.45	123	7
5.00	5.0	100	0
10.0	11.0	110	8
20.0	18.9	95	14
50.0	50	100	1
100	96	96	13
200	164	82	3
400	310	77	8
1000	480	48	17

Data taken from Reference 1.
These data are provided for guidance purposes only.

TABLE 3

EXAMPLE SPIKE RECOVERIES OF NITRATE AT FOUR DIFFERENT CONCENTRATIONS IN THREE GROUNDWATER SAMPLES

Spike Conc. (mg/L)	Mean Recovery (%)	Mean RSD (%)
2.00	113	10.7
3.00	106	7.6
5.00	98	1.2
10.0	89	2.7

Data taken from Reference 2.
These data are provided for guidance purposes only.

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