



Standard Test Methods for Continuous Determination of Sodium in Water¹

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1. Scope*

1.1 These test methods cover the continuous determination of trace amounts of sodium in water using an ion-selective electrode and flame photometry. Two test methods are included:

	Sections
Test Method A—Ion-Selective Electrode	8 to 16
Test Method B—Flame Photometry	17 to 26

1.2 Test Method A is based on continuous application of the sodium ion electrode as reported in the technical literature (1-3).² It is generally applicable over the range of 0.05 to 10 000 µg/L.

1.3 Test Method B is based on the use of flame photometry. It is most applicable to measurements below 20 µg/L. Compared with Test Method A, it is less vulnerable to interference from other monovalent cations at low concentrations and can reach equilibrium with very low sample throughput.

1.4 The analyst should be aware that adequate collaborative data for precision and bias statements as required by Practice D 2777 are not provided. See Sections 16 and 26 for details.

1.5 The values stated in SI units are to be regarded as standard. The inch-pound units given in parentheses are for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements see Section 6.

2. Referenced Documents

2.1 ASTM Standards:

D 1066 Practice for Sampling Steam³

D 1129 Terminology Relating to Water³

D 1192 Specification for Equipment and Sampling Water and Steam in Closed Conduits³

D 1193 Specification for Reagent Water³

D 1293 Test Methods for pH of Water³

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water³

D 3864 Guide for Continual On-Line Monitoring Systems for Water Analysis³

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

4. Significance and Use

4.1 Sodium is a pervasive contaminant and the first cation to break through deionization equipment. These test methods allow measurements of micrograms per litre (parts per billion) concentrations of sodium in water for monitoring low-sodium water sources for indications of contamination or proper operation. Applications include monitoring of demineralizer system performance and power plant boiler carryover and condenser leakage.

4.2 These test methods are more sensitive and selective than conductivity measurements on high purity samples.

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.⁴ In many instances, reagent grade chemicals contain higher levels of sodium contamination than are compatible with these test methods. It must be ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water

¹ These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.03 on Sampling of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water.

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² The boldface numbers in parentheses refer to the list of references at the end of these test methods.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

*A Summary of Changes section appears at the end of this standard.

conforming to Specification D 1193, Type I. In addition, the sodium or potassium content shall not exceed 10 µg/L (10 ppb) or 1 % of the lowest concentration to be determined, whichever is lower.

5.2.1 Single-distilled water passed through a mixed bed deionizing unit composed of strong cation and anion resins can produce an effluent containing less than 1.0 µg/L (1.0 ppb) of sodium. If such water is stored in a closed alkali metal-free container, such as one made of polyethylene, TFE-fluorocarbon, or stainless steel, subsequent increases in conductivity, usually due to absorption of carbon dioxide, will not invalidate its use for this purpose.

6. Hazards

6.1 *Test Method A*— pH adjusting reagents are strongly alkaline and volatile. Use normal eye and skin protection when handling ammonia, ammonium hydroxide, dimethylamine, diisopropylamine, monoethylamine, or morpholine. Extra care is needed in handling the gas-permeable tubing immersed in liquid reagents used with the passive diffusion reagent delivery system. Keep reagents in the open wherever possible and take necessary precautions to keep them from the respiratory tract in event of a spill or leak. Under certain conditions these reagents can produce an explosive mixture with air. OSHA standards must be followed.

6.2 *Test Method B*:

6.2.1 Use normal safety precautions in handling hydrogen and oxygen gas.

6.2.2 Use extreme care to avoid contact of skin with the extremely hot oxy-hydrogen flame as instant third-degree burns would result.

6.2.3 For unattended operation of flame photometer, provide means to ensure that flame gases are shut off quickly and automatically if the flame should be extinguished for any reason.

7. Sampling

7.1 Sample the water for continuous sodium ion measurements in a flowing stream in accordance with Practice D 1066, Specification D 1192, and Guide D 3864, as applicable.

7.2 Regulate the pressure of samples within the instrument manufacturer's requirements.

7.3 Regulate the temperature of samples that must be condensed, or cooled, or both, to a level between 15 and 40°C (59 and 104°F) or within manufacturer's requirements. For highest accuracy, bring the sample temperature close to the temperature of the standards during calibration.

7.4 When sample system plumbing has been newly installed, or has not been carrying process stream water for some time, or has been open to the atmosphere, it may take 24 h of purging to bring the sodium content at the receiving end down to the same level as the sample point, especially when the process stream is less than 1.0 µg/L (1.0 ppb). In the case of lines that are very dirty or have been subject to biological fouling, pumping a 25 % solution of nitric acid is effective for plastic and stainless lines. About 30 line-volumes of acid should be pumped through slowly, followed by the fastest practical purge of process water in the amount of 300 volumes. When using an acid-cleaning procedure, confine the acid to the

dirty part of the system. Under no circumstances should the acid enter the measuring instrument.

7.5 Adjust the sample flow in accordance with the manufacturer's recommendation.

7.6 Where speed of response is not critical, sequential sampling of multiple streams may be effected with 3-way solenoid valves for sample selection. The 3-way valves allow samples not being measured to continue flowing (to drain) and to be current when they are selected. Automatic selection should include an adjustable timing device for typical sampling times near 10 min per point.

TEST METHOD A—SODIUM ION ELECTRODE

8. Scope

8.1 This test method covers the continuous measurement of sodium in water using a sodium ion electrode.

9. Summary of Test Method

9.1 Sodium ion electrodes provide consistent logarithmic response over many orders of magnitude of concentration using the same principles as pH electrodes but with different ion selectivity. The electrode signal has a slope of approximately 59 mV/decade change in sodium ion concentration at 25°C (77°F).

9.2 Where electrode selectivity and the sodium concentration and pH of the sample require it, this test method includes provision for the addition of pH adjusting reagent to suppress hydrogen ion concentration and assure accurate electrode response to sodium. The lower limit for accurate measurement without reagent appears to be about 1 µg/L (1 ppb) in ammonia-treated power plant samples (4).

9.3 This test method is particularly adaptable to high purity water and is relatively free of interferences (1). The overall operating cost of this system is considerably less than that of continuous flame photometry, and it is more sensitive than electrical conductivity.

9.4 The repeatability of this test method is ±5 % of the reading.

10. Interferences

10.1 The sodium ion electrode, like all potentiometric electrode measuring systems, is responsive to changes in ion activity and not true concentration changes (that is, the response is to changes in concentration multiplied by an activity coefficient). However, as concentrations approach infinite dilution, activity coefficients approach unity and ion concentration and active ion concentration become very nearly equal.

10.2 The activity coefficient of sodium ion will vary with changes in the total ionic strength of the solution. Therefore, it is important to maintain either a low or constant ionic strength. A constant flow of pH adjusting reagent generally establishes a consistent ionic strength.

10.3 The sodium content of pH adjusting reagent, if delivered directly to the sample, must not be significant compared with the lowest concentration being measured. Any air contacting the sample must be sodium-free.

10.4 The sodium ion electrode is responsive to certain other monovalent cations. Interference by silver, lithium, hydrogen, potassium, ammonium, and other ions must be considered. The selectivity to interfering ions varies by electrode manufacturer. In the low-solids water to which this test method applies, silver and lithium ions are usually absent. Potassium ion, often contributed to the sample by the reference electrode, must be carried downstream away from the sodium ion electrode. Ammonium ion, present in many power plant samples, generally does not interfere with measurements greater than 1 µg/L (1 ppb). Measurements below 1 µg/L use a stronger base reagent that suppresses the ionization of ammonia.

10.5 Elevation of pH so that hydrogen ion concentration is 3 to 4 orders of magnitude lower than that for sodium generally makes the electrode response independent of variations in hydrogen ion concentration. Any of the reagents mentioned is satisfactory to increase the pH to a level such that the electrode is essentially insensitive to hydrogen ion, within sodium ranges specified by the manufacturer. Exceptional electrode selectivity allows some measurements in ammoniated power plant samples greater than 1 µg/L (1 ppb) sodium without further reagent addition.

10.6 When this test method is used without pH adjusting reagent, the sample pH and sodium concentration must be within the manufacturer's guidelines for the particular sodium electrode to assure accurate measurement.

10.7 The sodium ion electrode is not subject to interference from color, turbidity, colloidal matter, oxidants, and reductants.

11. Apparatus

11.1 *Measuring Instrument*—Use commercially available potentiometric specific ion monitors that have expanded-scale operation with adjustable ranges calibrated directly in sodium ion concentration units of micrograms per litre (parts per billion). Electrical output signals must be isolated from ground and from electrode input and may be scaled for logarithmic, linear, or bilinear ranges.

11.2 *Sodium Ion Electrode*—Use a commercially available sodium-sensitive electrode (sodium ion electrode). Because electrode selectivities vary among manufacturers, care must be taken that the electrode, reagent or lack of it, and sample conditions are compatible (see 10.4, 10.5, and 10.6).

11.3 *Reference Electrode*—Use a reference electrode compatible with the measuring electrode.

11.3.1 When the sodium ion electrode has a silver-silver chloride internal half cell, the reference electrode should be silver-silver chloride. When the sodium ion electrode has a calomel internal half cell, the reference electrode should be calomel. Dissimilar reference electrodes may be used provided adequate compensation is made electronically to correct for the difference between the measuring electrode and the reference electrode. If the reference electrode filling solution is an interference in the measurement of sodium, then the reference electrode must be downstream from the measuring electrode (see 10.4 and 11.3.2).

11.3.2 If calomel electrodes are used, refer to Test Methods D 1293. The electrolyte used in reference electrodes and all maintenance shall conform to the manufacturer's recommendations. With flowing junction reference electrodes to ensure

the desired slow outward flow of electrolyte, the solution pressure inside the junction shall be kept somewhat higher than that outside the junction.

11.4 *Temperature Compensation*—Use an automatic temperature compensator in accordance with the manufacturer's recommendation.

11.5 *Flow Chamber*—For best results install the electrodes in a flow chamber and take the measurement on a flowing stream. Use a flow chamber as recommended by the manufacturer. If otherwise, design the flow chamber to minimize interference from the reference electrode and construct the chamber of inert materials such as plastic or stainless steel.

11.5.1 If a plastic is used, cast or machine from a solid block. Gasket electrodes to prevent in-leakage of air. Protection of electrodes shall be in accordance with the manufacturer's recommendations. Connections to the flow chamber must be *solution* or *earth* grounded. No glass or copper is permissible in flow chamber construction.

12. Reagents and Materials

12.1 *pH Adjusting Reagents*:

12.1.1 *Ammonia Gas*—Commercial anhydrous grade ammonia (NH₃) having a minimum purity of 99.9 %. Gas is absorbed directly by the sample.

12.1.2 *Ammonium Hydroxide*—Commercial ammonia solution, approximately 29 % NH₃ in water. Vapor diffuses into the sample through an ion-impermeable membrane.

12.1.3 *Diisopropylamine*—Commercial grade liquid is vaporized and transported by an inert carrier gas to the sample stream.

12.1.4 *Dimethylamine Gas*—Commercial grade having a minimum purity of 99 %. Gas is absorbed directly by the sample.

12.1.5 *Monoethylamine*—Commercial grade vapor diffuses into the sample through an ion impermeable membrane.

12.1.6 *Morpholine-Containing Proprietary Buffer Solution*—From sodium analyzer manufacturer, maintained free of sodium and not stored in glass prior to use. Liquid is fed directly to the sample.

12.2 *Sodium Chloride Stock Solution* (1.00 mL = 0.100 mg Na)—Dissolve in water 0.2542 g of sodium chloride (NaCl), dried to constant weight at 105°C in water, and dilute to 1 L in a thoroughly cleaned polyethylene flask. Store sodium stock in a polyethylene or equally alkali metal-free container. Prepare standards of lesser concentrations by dilutions of the stock solution.

13. Calibration and Standardization

13.1 All procedures described in this section are subject to zero and calibration drift. Determine the frequency of calibration checks required to obtain the desired accuracy based on experience. Whenever a major shift in sodium concentration is noted, a calibration check is advisable.

13.2 Low sodium standards are subject to contamination from many sources. Calibrate using standards above 100 µg/L (100 ppb) to reduce the effects of contamination. To avoid most contamination connect the standard container to the measuring equipment so that the standard can be introduced without exposing it to nonfiltered air. Use manual or automatic valves

to introduce the standard for calibration checks. Some analyzers use a known increment method that employs higher level sodium standards.

13.3 Run the sample and pH adjusting reagent, if used, through the flow chamber for at least 12 h before attempting measurements or calibration (24 h when the equipment is new) to purge sodium contamination from all parts of the sampling and measuring equipment, especially valves. In systems where serious damage to the measuring electrode may occur if the sample flow is interrupted, provide means to automatically discontinue the pH adjusting reagent flow.

13.4 *Sodium Ion Measurement with pH Adjustment by Addition of Anhydrous Ammonia:*

13.4.1 In this procedure, pH adjustment is by continuous addition of ammonia to the continuously flowing liquid sample. The pH level is maintained relatively constant at pH 11.0 to 11.1. Provide a reasonably stable sample flow rate, sufficient to attain reasonable response time, but not so great as to unduly consume ammonia. Follow manufacturer's flow rate recommendations.

13.4.2 Pipe the standard sodium solution into the system to prevent contamination during calibration.

13.4.3 Turn on the instrument and allow it to warm up in accordance with the manufacturer's instructions.

13.4.4 Connect the analyzer to a water source expected to have sodium ion concentration below 10 µg/L (10 ppb). This may be demineralizer effluent or high quality process water. Start the water flow. Maintain the temperature of the sample below 40°C (104°F).

13.4.5 Allow the water to flow until a stable reading is obtained. For a new instrument this may be 24 h or more. It is extremely important that all new equipment and sample lines be thoroughly flushed to remove any residual sodium (see 13.3).

13.4.6 After a stable reading is obtained, calibrate the instrument according to the manufacturer's procedure.

13.5 *Sodium Ion Measurement with pH Adjustment by Addition of a Proprietary Buffer Solution Containing Morpholine :*

13.5.1 Prepare the standards such as those containing 1 mg/L (1 ppm) and 100 µg/L (100 ppb) of sodium ion by appropriate successive dilutions of the sodium chloride stock solution (see 12.2).

13.5.2 Turn the instrument on and allow it to warm up in accordance with the manufacturer's instructions.

13.5.3 Connect the electrode chamber to a temperature-regulated water source (see 7.3) with a sodium concentration below 10 µg/L (10 ppb). This may be demineralizer effluent, high-quality process water, or sample source. Start the water flow.

13.5.4 Regulate the flow of proprietary buffer solution containing morpholine, in accordance with the manufacturer's instructions, to provide a pH greater than 10.0.

13.5.5 Allow the water to flow until a stable reading is obtained. For a new instrument this may be 24 h or more. It is extremely important that all new equipment and sample lines be thoroughly flushed to remove any residual sodium (see 13.3).

13.5.6 After stable readings are obtained, set the instrument control on standby. Measure the standard including the buffer solution containing morpholine. Continue the water flow in accordance with the manufacturer's recommendations until a stable reading is obtained. Adjust the instrument to read the standard value. Repeat the entire procedure with other standards in order of increasing concentration until the highest expected sample concentration is included in the range.

13.5.7 After the instrument is calibrated for the highest concentration standard, flush the instrument with sample. After exposure to a high concentration sodium standard, an appreciable time may be required to flush electrode chamber of excess sodium.

13.6 *Sodium Ion Measurement with pH Adjustment by Passive Diffusion of Monoethylamine or Ammonium Hydroxide and Calibration by Known Increment Technique Double Known Addition (DKA):*

13.6.1 In this procedure, pH adjustment is accomplished by passive diffusion, wherein the sample passes through an ion impermeable tubing coil present in a reagent bottle containing monoethylamine or ammonium hydroxide, which diffuses through the tubing wall and redissolves, raising the sample pH to about 11, in the case of monoethylamine. Sample flow rate must be sufficient to attain reasonable response time. Manufacturer's sample flow rate recommendations must be followed.

13.6.2 Install the instrument according to manufacturer's instructions, allowing for adequate flushing of the fluidic system for stabilization before initial calibration and use.

13.6.3 Calibrate the instrument using a double known addition technique in which sample concentration and electrode slope are determined simultaneously. To calibrate the instrument using DKA, follow manufacturer's instructions for ensuring calibration concentration increments and flow cell volume are properly programmed into the monitor. Push in the diverter valve on the flow cell. The flow cell reservoir begins to fill. The liquid level will rise above the siphon inlet then begin to drop. Open calibration port of flow cell cap.

13.6.4 Follow manufacturer's instructions for pipetting two increments of standards into the calibration port of the flow cell. Upon completion, read the sodium value from display. Pull out diverter valve and reopen flow valve. Allow liquid to return to normal operating level.

13.7 *Sodium Ion Measurement with pH Adjustment by Addition of Diisopropylamine or Dimethylamine:*

13.7.1 In this procedure, pH adjustment is made by continuous addition of amine to the continuously flowing liquid sample. The pH level will be relatively constant at pH 11.0 to 11.5. Maintain sample flow rate sufficient to attain reasonable response time. Follow the manufacturer's amine and sample flow rate recommendations.

13.7.2 Pipe the standard sodium solution into the system to prevent contamination during calibration.

13.7.3 Turn the instrument on and make adjustments in accordance with the manufacturer's instructions.

13.7.4 Start the water flow. Keep the temperature of the sample below 40°C (104°F).

13.7.5 Allow the water to flow until a stable reading is obtained. Flush sample lines thoroughly to remove any residual sodium (see 13.3).

13.7.6 Calibrate either by direct adjustment to standard solutions made up by dilution of the sodium chloride stock solution (see 12.2) or by the *known increment* principle, a technique that depends on the unique logarithmic response characteristic of the sodium ion electrode (3). Follow manufacturer's procedures.

13.7.7 Discontinue the flow of calibration solution and return the instrument to the analysis of process water.

13.8 *Sodium Ion Measurement Without pH Adjusting Reagent:*

13.8.1 Where power plant samples are already near 9 pH, a sodium ion electrode with adequate selectivity can measure directly without reagent addition at 1 µg/L (1 ppb) and above.

13.8.2 Follow the steps in 13.7, except for reagent flows. Make up standard solutions by dilution of sodium chloride stock solution (see 12.2), including manufacturer's recommendations for pH adjustment of the standards.

13.9 *Electrode Treatment*—Condition and maintain new sodium ion electrodes and those that have been stored dry as recommended by the manufacturer. If the assembly is for intermittent use, keep it filled with water and the electrodes immersed between measurements.

13.10 *Flow Chamber Treatment*—On a new electrode chamber or one that has been inoperative for a prolonged period, flushing of the system with sample or with demineralized water of the highest purity attainable is recommended before measurements are made. Flushing for 24 h or more may be necessary to remove traces of sodium from newly installed equipment and tubing (see 7.4).

13.11 *Standard Reservoir*—Make provisions for introduction of a sodium standard. Provision can be made to permit draining of the flow chamber before the standard is introduced. Stainless steel or plastic valves are recommended. The standard storage reservoir must be of material that does not contribute sodium. Glass is not permissible. Either polyethylene bottles or bags, acid-washed and rinsed with water, are recommended for storage. Vent or pressurize the container in such a manner as to prevent contamination of the standard.

14. Procedure

14.1 After calibration and standardization as instructed in 13.4, 13.5, 13.6, 13.7, or 13.8, maintain reagent addition, if used, and direct the sample flow to the electrodes. Record data continuously or manually until the run is completed.

15. Response Time

15.1 The response time of the system is determined by two independent factors: the length of time required for a unit volume of new solution to flow through the system and completely rinse out the previous solution, and the response time of the sensing electrodes themselves. The use of filters will greatly increase the time of response depending on the size and type. Upscale response time is generally much faster than downscale.

16. Precision and Bias

16.1 Neither precision nor bias data can be obtained for this test method from a collaborative study because this test method is a continuous determination. No suitable means has been found of performing a collaborative study to meet the requirements of Practice D 2777. This inability to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D 2777.

16.2 Statistical data on sodium measurements employing passive diffusion and double known addition techniques in power plants has been obtained as part of EPRI project RP2712-3 (5).

TEST METHOD B—FLAME PHOTOMETRY

17. Scope

17.1 This test method covers the continuous measurement of sodium in water using flame photometry.

18. Summary of Test Method

18.1 When a solution containing salts of sodium is atomized into a gas flame, light that is characteristic of, and highly specific to, sodium is emitted with the intensity being a function of concentration. The flame photometer consists of apparatus for giving a reproducible amount of emitted light for a given concentration of sodium in the test solution and for determining the intensity of such radiation.

18.2 Sample handling apparatus allows continuous monitoring of a single sample stream or alternate/sequential monitoring of more than one stream, using one flame photometer.

18.3 The advantageous range of application of this test method as compared to the use of Test Method A will be:

18.3.1 Where the range of sodium concentration is below 20 µg/L (20 ppb), which is near the upper linearity limit for this test method.

18.3.2 Where the most important range of concentration is below 1.0 µg/L (1.0 ppb) and interferences from other monovalent cations may render the readings of Test Method A questionable.

18.3.3 Where equilibration of the instrument reading in either the shortest possible time or with the least throughput of sample is desirable. This will be an important consideration when sample concentration is changed from high (>10 µg/L) to low (<1.0 µg/L).

18.4 At ranges above 1.0 µg/L (1.0 ppb) and where sample throughput is of little consequence, Test Method A will probably be the test method of choice, because of relative freedom from operator attention and absence of fuel consumption. There are also more variables in Test Method B that entail a higher degree of operator competence.

19. Interferences

19.1 In the analysis of low-solids water, radiation interferences caused by elements other than sodium are negligible.

19.2 The principal errors encountered are variations in flame background and contamination of the flame by airborne dusts. Because of the abundance of sodium in all atmospheric dust, filter air entering the burner housing. Allow no smoking in the vicinity of the photometer since cigarette smoke is

heavily contaminated with sodium and potassium. Equipment and procedures for minimizing these effects are described in 20.2.

20. Apparatus

20.1 *Flame Photometer*— The instrument shall consist of an atomizer/burner in a closed housing that is purged with high-purity air, a continuous-flow sample system to deliver 25 mL/min sample to the atomizer and accommodate the overflow, and a spectrophotometer capable of measuring the 589 nm emission from the flame. Flame gas supply and control apparatus shall be arranged to provide a stable flame.

20.1.1 A spectrophotometer with a grating monochromator is mandatory for work below 1.0 µg/L (1.0 ppb) as the bandpass should be 1.0 nm or less, with slit width not so low as to require photomultiplier voltage above 650. The entire optical system should be optimized to provide fairly flat response of photomultiplier output versus wavelength for the range 570 to 610 nm. Further information is provided in Appendix X1.

20.2 *Blower and Air Filters*—Pressure and volume capabilities must constantly purge the burner chamber with sodium-free air.⁵

20.3 *Recorder*—To be compatible with the output of the spectrophotometer and have a chart speed sufficient to separate the sample signals clearly.

21. Reagents and Materials

21.1 *Sodium Chloride Solution, Stock*—See 12.2.

21.2 *Hydrogen Gas, sodium-free.*

21.3 *Oxygen Gas, sodium-free.*

NOTE 1—The normal welding grades of gases have been found quite satisfactory. However, if extensive supply lines are used, microparticulate filters are advised to be installed just prior to connection to the instrument.⁶

22. Sampling

22.1 See Section 7.

22.2 The burners in common use will aspirate from 1 to 5 mL/min. Delivery of sample to the burner should be at the rate of 10 to 25 mL/min to give short equilibration times. Thus, there will be some overflow of sample to waste. To accommodate these flow requirements a simple weir block will suffice. Delivery of the sample to the weir block can be by direct pressure from the process stream, or by means of a small peristaltic pump acting on plastic tubing.

22.3 *Effect of Sampling System on Speed of Response*—Where samples must be taken at widely separated points, attention must be paid to the rate at which the sample is withdrawn from the stream, in comparison to the volume of the line between the sample point and the instrument. The quotient of line volume divided by line flow rate will be a first-order time constant, and thus limit the speed of response. Also,

consider the adsorptive characteristics of the tubing material; any surface absorption and desorption of sodium ions will increase equilibration time. If the operating environment will permit plastic lines (PVC, polypropylene, or polyethylene), these will be found to be easiest and cheapest to install, and they exhibit low retention of sodium.

22.4 All sample lines terminating at the instrument should be allowed to flow freely whether or not they are delivering sample to the instrument at any particular time. This will keep all sodium concentrations current and help to prevent settling of particulate matter in pockets or tubing joints.

22.5 Requirements for sampling solenoid valves are made more stringent if there is appreciable upstream pressure when they are off. A gravity overflow weir upstream of the solenoid valve, with gravity delivery of sample to the instrument, will enable valves of modest capability to exhibit the necessary leak-free performance.

22.6 For sampling the calibrations standards, reagent water (blank), or occasional grab samples, a peristaltic pump acting on plastic tubing is most appropriate.

23. Calibration and Standardization

23.1 Calibration in range 0 to 20 µg/L (0 to 20 ppb) with grating-type instrument with bandpass of approximately 1 nm, and photomultiplier detector:

23.1.1 Prepare at least three standards, by dilution of a stock solution of at least 10 mg/L (10 ppm). See 12.2 and Note 2 for preparation of stock and standard solutions, respectively. The concentration of the standards will depend on the range in which the instrument is to be calibrated, but in general, the standard values selected should give points on the calibration curve in the lower, middle, and upper thirds of the full-scale range. When making dilutions into the 0 to 20 µg/L (0 to 20 ppb) range, errors due to contamination will be difficult to avoid. Sample and standard handling vessels and pipettes should be of plastic, not glass.

23.1.2 Turn on the electrical power to the instrument, feed fuel and oxygen to the burner and ignite the flame. Set fuel and oxygen pressures or other flow parameters to manufacturer's recommended values. Let instrument electronics and burner stabilize according to manufacturer's recommendations while purging the system with water.

23.1.3 On instruments where coarse sensitivity is controlled by photomultiplier voltage, set coarse sensitivity control so that dry flame (not aspirating water) background reading above electrical zero is in the vicinity of 2.5 µg/L (2.5 ppb), more or less, as optical bandpass is greater or less than 1.0 nm, respectively. Electrical zero is defined here as the detector output, including dark current with light from flame blocked, and with normal operating voltage on photomultiplier.

23.1.4 Aspirate water, and when reading is stable at 589 nm, take readings at 5 or 6 nm above and below 589 nm. Take several readings at each wavelength to determine if burner has stabilized. If the reading at the longer wavelength is higher than the reading at the shorter one, adjust the zero control so that the readout indicates one-half the difference between readings, positive, at the longer wavelength. If the reading at the shorter wavelength is higher than that at the longer

⁵ Donaldson Corp., Minneapolis, MN, space air filter Type HEPA 82141-Flanged Ultra has been found satisfactory for this purpose.

⁶ Balston Corp., Lexington, MA, microparticulate filter Type 92 BX Cartridge and Type M92-810 Housing have been found satisfactory for this purpose.

wavelength, adjust the zero control so that the readout indicates one-half the difference between readings, positive, at the shorter wavelength.

23.1.5 Aspirate the maximum value standard, and set the wavelength for maximum indication on readout. Adjust the fine sensitivity control to make reading close to the value of the standard. Do not touch wavelength setting for the remainder of the calibration procedure.

23.1.6 Aspirate water (blank), and when reading is stable, record the indicated value. Noise and fluctuation of the reading should not exceed 0.04 µg/L (0.04 ppb), peak to peak. Aspirate the standards in ascending order of sodium concentration, and record the readings.

23.1.7 Plot the readings obtained in 23.1.6 on linear paper with readings as ordinates and standard concentrations as abscissae; a straight line will be the ideal result. If the line is not straight, the errors may be from dilution, or they may be instrumental. Extreme departure from linearity, within the range of the standards, is most likely due to contamination error in the dilution, and a new set of standards should be prepared. When a repeatedly straight line has been achieved the slope of plot, or the average of the slopes of the segments of the plot, can be calculated, and the sodium content of the water can be found by dividing the reading for the water by this slope. Adding the value thus found to the values of the standards will enable accurate assignment of standard concentrations and final calibration of the readout indication directly in micrograms per litre (parts per billion).

NOTE 2—When stock solutions are diluted with water, at each stage of dilution, the resultant sodium concentration will be that of the stock, or previous dilution, divided by the dilution factor, plus the sodium concentration of the water.

For example: 1000 mg/L (ppm) Standard diluted 1000:1 with water of 0.5 µg/L (ppb) sodium content gives:

$$\frac{1000 \text{ mg/L}}{1000} + 0.0005 \text{ mg/L} = 1.0005 \text{ mg/L} = 1000.5 \text{ µg/L}$$

Diluting this solution 100:1 to make a working standard gives:

$$\frac{1000.5 \text{ µg/L}}{100} + 0.5 \text{ µg/L} = 10.505 \text{ µg/L}$$

Because the last significant figure in this calculation represents precision well outside the capability of the present instrumentation to achieve, it will be seen that the effect of water sodium content will be measurable only at the last stage of dilution.

In practice then, the calibration of commercially available instrumentation amounts to a determination of water sodium content by the method of standard additions, with the instrument scale factor calibration and adjustment coming only as an ancillary result. This curious state of affairs arises because water with zero sodium content is presently very difficult, if not impossible to obtain. The best water from distillation followed by recirculation through multiple deionizing resin beds will measure, by this test method, at about 0.05 µg/L (0.05 ppb) with uncertainty of ±0.03 µg/L (0.03 ppb).

23.1.8 When the sodium content of the water has been determined, add this value to the concentration value of the highest standard, and while aspirating this high standard, adjust the fine sensitivity control to make the readout indicate this

(assigned) true value of sodium content. The instrument is now calibrated for direct reading, in range 0 to 20 µg/L (0 to 20 ppb).

23.2 Calibration in Range 0 to 200 µg/L (0 to 200 ppb):

23.2.1 With the oxygen/hydrogen burner and a simple lens system to image the flame onto the monochromator entrance slit, pronounced nonlinearity is observed for readings of standards above 20 µg/L (20 ppb), that is, the readings increase more slowly with increased sodium concentration. It is expected that the degree of nonlinearity will vary somewhat with changing amounts and ratios of hydrogen and oxygen in the flame. For that reason, calibration curves with standards up to 200 µg/L (200 ppb) may not repeat well from day to day unless strict attention is given to the flame gas ratios and amounts. Also, uptake rate of the burner may have some effect. The probable reason for this behavior is that with high sodium concentrations the outer portions of the flame will contain cool, unexcited sodium vapor that then is involved in self reversal or atomic absorption. This phenomenon of self reversal is most easily demonstrated in the sodium line emission from a spectrographic carbon arc in which there is a pronounced temperature gradient through the arc cross section.

23.2.2 At high concentrations the high temperature of the arc will cause a large amount of Doppler-broadened energy to be seen visually at the focal plane of the spectrograph and through a magnifying glass the lines will appear quite broad, yet the central portion of the lines within 0.03 nm of the true center wavelength will be quite dark. The calculations necessary to standardize the instrument in the 0 to 200 µg/L (200 ppb) range are illustrated in 25.1.

NOTE 3—The type of instrument with fixed slit width and sensitivity varied by control of the photomultiplier voltage has many operational advantages over the instrument where sensitivity can only be varied (over a small range) by means of the slit width. The approximate photomultiplier voltage can be ascertained as in 23.1.3 and set to a round, easily remembered value. This is a coarse sensitivity adjustment and need not be changed over long periods of time. If the electrical zeroing is accomplished by applying a variable current to the amplifier at its input and in opposition to the current from the photomultiplier, a small amount of electrical gain control over a range of approximately four to one in sensitivity can be easily arranged at some point electrically *downstream* of the amplifier input. Properly applied, this later control will have no effect on the *zero* reading, and once the procedure in 23.1.7 is performed to determine the most probable sodium zero point, the *fine* gain, span, or sensitivity control can be adjusted to give reading of (standard and water blank) without affecting the zero reading. Of course, it must be noted that the best water available will have a sodium content around 0.05 to 0.07 µg/L (0.05 to 0.07 ppb) and that *zero* indications will not be observed under usual laboratory conditions.

24. Procedure

24.1 Generally the procedure for samples will differ from that for standards only according to the requirements and limitations of the sample system plumbing. Where an extensive manifold system arranged for selecting one of several sample streams is used, purge with currently selected sample to eliminate all of the previous sample. When the current sample is below 1 µg/L (1 ppb) sodium content, purge for 1 min or more, as necessary. A strip chart recorder trace will give the clearest picture of the state of equilibration.

25. Calculation

25.1 If the calibration has been carried out so that the instrument readings are directly in micrograms per litre (parts per billion), no calculations are required below 20 µg/L (20 ppb). For values read between 20 and 200 µg/L (200 ppb), with bracketing standards S_1 and S_2 giving readings Y_1 and Y_2 , if Y is reading of unknown X , then:

$$X = Y_1 + \frac{(Y - Y_1)(S_2 - S_1)}{(Y_2 - Y_1)}$$

The arithmetic is a linear interpolation on a piecewise approximation to the true curve, and because the segments of the approximation lie below the true curve, the resultant values will be lower than the true values insofar as the measured values fall further away from the bracketing standards.

26. Precision and Bias

26.1 Neither precision nor bias data can be obtained for this test method from a collaborative study because this test method

is a continuous determination. No suitable means has been found of performing a collaborative study to meet the requirements of Practice D 2777. This inability to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D 2777.

26.2 In the range over 200 µg/L, users report typical single operator precision of 5 to 10 % of the reading.

26.3 In the range of 1 to 20 µg/L, users report typical single operator precision of 1 to 2 µg/L.

26.4 Below 1 µg/L, single operator precision is typically 1 to 2 times the detection limit.

27. Keywords

27.1 continuous sodium measurement; flame photometry; ion-selective electrode; specific ion

ANNEXES

(Mandatory Information)

A1. CONSTRUCTION OF pH ADJUSTMENT SYSTEMS FOR TEST METHOD A

A1.1 Anhydrous Ammonia

A1.1.1 A system for anhydrous ammonia addition to the sample shall be constructed as follows: Use a commercially available ammonia regulator on the ammonia cylinder. Immediately downstream of the regulator install a filter (5-µm stainless steel filter element). Downstream of the filter install a check valve and a needle valve. A flow meter or capillary shall be used between the needle valve and point of addition. A capillary can be used where ammonia enters the mixing tee. Stainless steel or plastic fittings and tubing should be used throughout. The standard solution connection and drain or bypass valve shall be installed in the sample line upstream of the ammonia addition point.

A1.2 Morpholine

A1.2.1 Place buffer solution containing morpholine in a container that is elevated, or pressure it with 35 kPa (5 psig) clean, dry, sodium-free air. Adjust the buffer solution flow to 0.5 mL/min by means of a valve or by adjusting length and size of the capillary tubing.

A1.3 Dimethylamine

A1.3.1 Sample water having a temperature of 15 to 40°C (59 to 104°F) passes through a regulator and block valve.

Sample flow rate is indicated and controlled by a flow meter-needle valve combination. Gaseous dimethylamine from a cylinder is regulated and supplied to a mixing (absorber) column where sample pH is elevated to 11.0 to 11.5. The conditioned sample enters a baffled flow chamber where an electrode system consisting of a sodium-ion electrode, reference electrode, and an automatic temperature compensator produce a voltage output proportional to the logarithm of sample sodium ion activity. The signal is displayed on an indicating monitor. Voltage and current outputs from the monitor are used for analog recording or data acquisition.

A1.4 Diisopropylamine

A1.4.1 The system for diisopropylamine addition is similar to that for dimethylamine addition described in A1.3. One exception is noted. Diisopropylamine liquid is contained in a 5-gal reagent vessel. A gas-vapor transport technique using dry nitrogen carrier gas conveys the diisopropylamine to the mixer (absorber) column where sample pH is adjusted to 11.0 to 11.5.

A1.5 Ammonium Hydroxide or Monoethylamine Solution

A1.5.1 The reagent solution is held in a container with a length of gas-permeable rubber tubing carrying the sample through it.

A2. ELECTRODE RESPONSE IN TEST METHOD A

A2.1 Faulty Electrode Response

A2.1.1 The sodium ion measuring assembly should be calibrated periodically with two reference standards to check the linearity of response of the electrode combination at different sodium ion concentrations and to detect a faulty sensing or reference electrode. A faulty sensing electrode is indicated by failure to obtain a correct value of sodium ion concentration on a second standard after the meter has been standardized with the first one. Special care must be taken with regard to handling and contamination of reference standards and pH adjustment of standards as described in 5.1, 5.2, 10.3, 10.4, and Section 13.

A2.1.2 Contamination or inadequate pH levels can also result in insufficient response between two calibration standards and unfounded suspicion of measuring electrode failure.

A2.2 Impaired Electrode Response

A2.2.1 The sodium ion responsive properties of the glass sensing electrode may be impaired by substances such as oily materials and precipitates. Normally such substances will not be present in appreciable quantities in low-solids water except possibly during startup of new equipment or in cycling power plants.

A2.3 Electrode Cleaning Techniques

A2.3.1 When an electrode is suspected of being coated by oily substances or insoluble precipitates, or both, its usefulness can normally be restored by appropriate cleaning procedures. Oily matter can generally be removed by solvents such as

alcohol (7 parts ethanol, 3 parts water). Precipitates or insoluble inorganic coatings can normally be removed by immersing the bottom third of the electrode in hydrochloric acid (1 part concentrated HCl (sp gr 1.19), 9 parts water). After either solvent or acid cleaning, the electrode should be rinsed thoroughly with a flowing stream of Type I or other high-purity water. Following this rinsing, the electrode should be installed in the electrode chamber and flushed at least 2 h with pH adjusted water or until a stable reading is obtained. It should then be rechecked with two known reference standards.

A2.3.2 If faulty response is still obtained after replacement of a suitably conditioned sodium electrode, as indicated by failure to give satisfactory readings with two known sodium standard solutions, the reference electrode, measuring instrument, and temperature compensator (if automatic type) should be examined for maloperation. These systems occasionally need service and should always be thoroughly checked if replacement of the sodium electrode does not improve measurements.

A2.4 Temperature Compensation

A2.4.1 The sodium ion electrode and reference electrode pair shall be operated only on samples within the temperature range recommended by the manufacturer. An automatic temperature compensator as supplied by the manufacturer for use with the sodium-sensitive electrode shall be installed in the flow chamber along with the sodium sensitive electrode and reference electrode.

APPENDIX

(Nonmandatory Information)

X1. SPECTROPHOTOMETER CHARACTERISTICS

X1.1 For spectrophotometers equipped with variable slits, consideration must be given to the fact that the intensity of the sodium emission line, as seen by the detector, is approximately proportional to the slit width whereas the continuous background emission intensity varies as the square of slit width. The wavelength dispersing power of the monochromator (nm/mm of slit width) should be such that slit width of 0.2 to 0.5 nm gives an optical bandpass of 1 nm. The emission of sodium at 589 nm consists of two lines separated by 0.6 nm, so that resolution better than 1 nm will tend to exclude one of these lines, resulting in less favorable optical throughput and more critical wavelength setting. The slit width requirement is imposed solely to keep photomultiplier voltage low enough so that dark current variations and dark current noise will be negligible, allowing a simpler electronics scheme.

X1.2 The above considerations practically rule out use of prism type monochromators as their dispersion is so low as to

give slit widths of 0.03 nm for 1 nm resolution at 589 nm. The usual slit widths used with prism type monochromators for sodium analysis result in about 10 times more background light for a given amount of sodium radiation, and the background light has a noise component that may approach the equivalent radiation of 0.1 µg/L (0.1 ppb) of sodium.

X1.3 Background radiation appears to be a fairly flat continuum extending from 200 nm to 700 nm. Its intensity in the region of 589 nm is somewhat dependent on hydrogen and oxygen flow ratios, but is quite strongly dependent on the flame temperature as influenced by water aspiration rate. Results of many tests of a grating type instrument with focal length 250 mm, dispersion of 3.2 nm/mm, and a slit width of 0.3 mm, which give an optical bandpass at 589 nm of 1 nm as follows:

Dry flame equivalent radiation at 589 nm	2.5 µg/L (ppb) Na
Wet flame equivalent radiation 8 mL/min water	0.6 µg/L (ppb) Na
Wet flame equivalent radiation 2 mL/min water	1.6 µg/L (ppb) Na

Short term pk-pk noise (1/s) wet & dry flame

0.02 µg/L (ppb) Na

X1.4 The dispersion at 589 nm of a 500 mm FL quartz prism monochromator is 33.5 mm/mm, thus the optical band-pass with 0.3 mm slits is about 10 nm and the above figures for

equivalent emission intensity will be multiplied by about 10, thus the resultant figure for the noise, 0.2 µg/L (0.2 ppb), puts a severe restriction on the lower limit of sodium that can be measured.

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SUMMARY OF CHANGES

This section identifies the location of selected changes to these test methods that have been incorporated since the last issue. For the convenience of the user, Committee D-19 has highlighted those changes that may impact the use of these test methods. This section may also include descriptions of the changes or reasons for the changes, or both.

(1) Test Method A now includes coverage of options for

measuring without reagent and with pH adjustment using ammonium hydroxide and monoethylamine reagents.

(2) Test Method B was revised and reinstated.

(3) The overall document was extensively revised and reorganized to reflect current technology and practice, current test method format, and to combine the two test methods.

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