



Designation: D2791 – 07

Standard Test Method for On-line Determination of Sodium in Water¹

This standard is issued under the fixed designation D2791; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the on-line determination of trace amounts of sodium in water using an ion-selective electrode.

1.2 This test method is based on on-line application of the sodium ion electrode as reported in the technical literature (1-3).² It is generally applicable over the range of 0.01 to 10 000 $\mu\text{g/L}$.

1.3 The analyst should be aware that adequate collaborative data for precision and bias statements as required by Practice D2777 are not provided. See Section 16 for details.

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

1.5 *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:³

- D1066 Practice for Sampling Steam
- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D1293 Test Methods for pH of Water
- D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D3864 Guide for Continual On-Line Monitoring Systems for Water Analysis

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

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

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

D3370 Practices for Sampling Water from Closed Conduits
D5540 Practice for Flow Control and Temperature Control
for On-Line Water Sampling and Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

4. Significance and Use

4.1 Sodium is a pervasive contaminant and it is the first cation to break through deionization equipment. This test method allows measurement of micrograms per litre (parts per billion) concentrations of sodium in water to monitor low-sodium water sources for indications of contamination or proper operation. Applications include monitoring makeup systems, condensers, condensate polishers, feedwater, boilerwater, and steam.

4.2 This test method is 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 this test method. 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 conforming to Specification D1193, Type I. In addition, the sodium or potassium content shall not exceed 10 $\mu\text{g/L}$ (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

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

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 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 exposed to 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.

7. Sampling

7.1 Sample the water for on-line sodium ion measurements in a flowing stream in accordance with Practice **D1066**, Guide **D3864**, Practice **D3370** and **D5540** 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. It is not advisable to sequence sample streams of significantly different concentrations using sequential sampling.

8. Summary of Test Method

8.1 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).

8.2 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).

8.3 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 on-line flame photometry, and it is more sensitive than electrical conductivity.

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

9. Interferences

9.1 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.

9.2 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.

9.3 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.

9.4 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.

9.5 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.

9.6 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.

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

10. Apparatus

10.1 *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.

10.2 *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 9.4, 9.5, and 9.6).

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

10.3.1 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 9.4 and 10.3.2).

10.3.2 If calomel electrodes are used, refer to Test Methods D1293. 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.

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

10.5 *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.

10.5.1 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.

11. Reagents and Materials

11.1 *pH Adjusting Reagents*:

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

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

11.1.3 *Diisopropylamine*—Commercial grade liquid is vaporized and transported by an inert carrier gas to the sample stream, or vapor diffuses into the sample through an ion-impermeable membrane.

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

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

11.2 *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.

12. Calibration and Standardization

12.1 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.

12.2 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.

12.3 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.

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