



# Standard Practice for On-Line Determination of Cation Conductivity in High Purity Water<sup>1</sup>

This standard is issued under the fixed designation D 6504; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice describes continuous sample conditioning by hydrogen ion exchange and measurement by electrolytic conductivity. It is commonly known as cation conductivity measurement in the power industry although it is actually an indication of anion contamination in high purity water samples. Measurements are typically in a range less than 1  $\mu\text{S}/\text{cm}$ .

1.2 The actual conductivity measurements are made using Test Method D 5391.

1.3 This practice does not provide for separate determination of dissolved carbon dioxide. Refer to Test Methods D 2186 and D 4519.

1.4 *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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

- D 1066 Practice for Sampling Steam<sup>2</sup>
- D 1125 Test Methods for Electrical Conductivity and Resistivity of Water<sup>2</sup>
- D 1129 Terminology Relating to Water<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>2</sup>
- D 2186 Test Methods for Deposit-Forming Impurities in Steam<sup>3</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>2</sup>
- D 3864 Guide for Continual On-Line Monitoring Systems for Water Analysis<sup>2</sup>
- D 4519 Test Method for On-Line Determination of Anions and Carbon Dioxide in High Purity Water by Cation Exchange and Degassed Cation Conductivity<sup>2</sup>

D 5391 Test Method for Electrical Conductivity and Resistivity of a Flowing High Purity Water Sample<sup>2</sup>

D 5540 Practice for Flow Control and Temperature Control for On-Line Water Sampling and Analysis<sup>2</sup>

## 3. Terminology

3.1 *Definitions*— For definitions of terms used in this practice, refer to Test Methods D 1125, Terminology D 1129, and Practice D 3864.

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *cation conductivity, n*—the parameter obtained by conditioning a sample by passing it through a hydrogen form cation ion exchange resin column and then measuring its electrolytic conductivity, on-line.

3.2.2 *specific conductivity, n*—direct electrolytic conductivity measurement of a power plant sample, usually dominated by treatment chemicals, such as ammonia or amines.

## 4. Summary of Practice

4.1 The sample is passed continuously through a small cation exchange column in the hydrogen form, which exchanges all cations for  $\text{H}^+$ . In this process, pH adjusting treatment chemicals, such as ammonia and amines are removed.

4.2 Measurement is made continuously on the conditioned sample with a process high purity conductivity analyzer/transmitter.

4.3 Temperature conditioning of the sample and specialized compensation of the measurement are used to minimize temperature effects on the performance of the ion exchange resin and the measurement.

4.4 Few studies have been published on the performance of cation conductivity measurement but one collaborative effort provides some background (**1**).<sup>4</sup>

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D-19 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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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.02.

<sup>4</sup> The boldface numbers given in parentheses refer to a list of references at the end of this standard.

## 5. Significance and Use

5.1 Cation conductivity provides one of the most sensitive and dependable on-line means of detecting anionic contamination in the boiler/steam cycle, such as chlorides, sulfates, nitrates, bicarbonates, and organic acids, such as formic and acetic.

5.2 High sensitivity is provided by intentionally eliminating the pH adjusting treatment chemical(s), for example, ammonia and amines, from the sample and converting remaining salt contaminants into their acid forms which are approximately three times as conductive.

5.3 Guidelines on cation conductivity limits for various cycle chemistry and boiler types have been established by EPRI (2-4) and by ASME (5,6).

5.4 The sample effluent from the cation exchange column also may be used, and in some cases is preferred, for ion chromatography or other anion measurements.

## 6. Interferences

6.1 Some weakly ionized cations may not be completely exchanged by the resin. This will produce positive or negative errors in the measurement depending on the sample composition. These errors can reduce sensitivity to corrosive contaminants.

6.2 Temperature effects on the cation resin may alter its equilibrium properties. Control sample temperature within the resin manufacturers' temperature limits to obtain consistent results.

6.3 The large temperature effects of high purity conductivity measurement must be minimized by sample conditioning and temperature compensation. Although sample temperature may be controlled closely, it may be significantly influenced by the ambient temperature as it passes through the column, tubing and flow chamber. The temperature coefficient of pure water is near 5 % of measurement per °C at 25°C, which can contribute substantial errors if not compensated properly. Temperature compensation must be appropriate for the unique acidic composition of cation conductivity samples. Conventional high purity temperature compensation for neutral mineral contaminants is not suitable for this application (7,8). The user is cautioned that the accuracy of algorithms for cation conductivity compensation may vary widely. The user should determine the applicability and accuracy of the instrument's temperature compensation in the anticipated temperature range.

6.4 Carbon dioxide may be in a sample and will be converted to carbonic acid and raise cation conductivity. This is not strictly an interference; however, carbon dioxide generally is not as corrosive as mineral salts and enters the cycle by different means. Where it is commonly present it may be desirable to obtain a cation conductivity measurement with carbon dioxide removed (see Test Methods D 2186 and D 4519).

6.5 Carbon dioxide may also be aspirated as a component of air, into the sample line through loose fittings in the exchange column, flowmeter, valves, etc. This is not representative of the actual sampling point and produces positive errors.

6.6 Incompletely regenerated or inadequately rinsed resin will release trace ionic impurities that produce positive errors.

The use of fresh resin completely in the hydrogen form and thoroughly rinsed is recommended. An exhausted resin column will have the same effect but with more rapidly increasing errors.

6.7 Fouled resin can leach conductive components even with an absolutely pure influent sample. Fresh resin is recommended.

6.8 Some cation resins contain leachables which can raise background conductivity and reduce sensitivity to sample impurities. Extensive rinsing usually is required. A continuous rinsing scheme is given in Appendix X1.2. Some success also has been achieved with a hydrochloric acid (1+4) pre-rinse.

6.9 For interferences with basic high purity conductivity measurements, refer to Test Method D 5391.

## 7. Apparatus

### 7.1 Cation Exchange Column:

7.1.1 The cation exchange column shall have an inside diameter of less than 60 mm (2.4 in.) and produce a flow velocity greater than 300 mm/min (1 ft/min) at the sample flow rate (see Appendix X1). The column shall have end screens to distribute flow across the cross-section of the column and to prevent resin beads and fines from escaping. The column may be piped for upward or downward flow. Upward flow provides automatic purging of air at startup which is helpful in cycling plants. However, the resin must be packed full to prevent fluidizing and channeling. Downward flow eliminates the possibility of fluidizing but requires the means to vent air from the column at startup. Care must be exercised to eliminate all air pockets which could cause channeling. The column should be constructed of nonleaching material, such as polycarbonate or polypropylene. Materials, such as polyvinylchloride, may leach chlorides and are not recommended. Flexible tubing used to make connections to the column should have minimal length and diameter to minimize the amount of leaching and air (carbon dioxide) permeation.

7.1.2 The resin shall be a sulfonated styrene-divinylbenzene with at least 8 % cross-linkage, strong acid gel cation exchange resin in the hydrogen form, filling the column. An indicating resin which changes color as its hydrogen ions are displaced is strongly preferred for convenient monitoring of the progress of resin exhaustion through the column.

7.1.3 The resin must be rinsed to remove leachables before full sensitivity can be reached. A convenient arrangement of multiple resin columns to provide the rinse and for easy change-out is described in X1.2.

7.2 *Process Sensor*—The conductivity cell shall be suitable for measurement of high purity water and shall include an integral temperature sensor for simultaneous temperature measurement within the cell volume. The temperature measurement shall be used for compensation in the instrument as described in 6.3 and in Test Method D 5391. The cell shall be housed in a small volume flow chamber to provide fast response.

7.3 *Process Instrument*—The instrument shall provide measurement, indication and temperature compensation as described in 6.3 and Test Method D 5391. It also may include alarm relays and analog or digital output signals as required by the application.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall 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.<sup>5</sup> 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.

8.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

8.3 *Hydrochloric Acid (1 + 4)*—Mix one volume of concentrated HCl (sp gr 1.19) with 4 volumes of water.

## 9. Sampling

9.1 For sampling refer to Practices D 1066, D 3370, and D 5540, as well as Test Method D 5391. Cation conductivity is one of the highest purity, lowest conductivity measurements in a power plant, and therefore, is vulnerable to trace contamination. Care should be exercised in closely following proper sampling techniques.

## 10. Calibration

10.1 For calibration refer to Test Methods D 1125 and D 5391.

<sup>5</sup> *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.

## 11. Procedure

11.1 Connect the apparatus as shown in Fig. 1 or X1.2, for continuous sampling and measurement. Follow the column manufacturer's instructions for purging air from the cation exchange column.

11.2 Set sample and bypass flowrates as needed to provide sufficient sample velocity in the main sample line and the recommended sample flow through the column. See 7.1.1, X1.1 and manufacturer's instructions.

11.3 Measure conductivity continuously, referring to Test Method D 5391.

11.4 Monitor for resin exhaustion. With indicating resin, note color change and replace the column when 75 % of the column length has been exhausted. With conventional resin, keep a record of the total time, flow, and specific conductivity values of the sample during the exchange life of the resin. Use this for scheduling future resin replacement well before exhaustion.

## 12. Keywords

12.1 boiler cycle chemistry; cation conductivity; on-line; process measurement

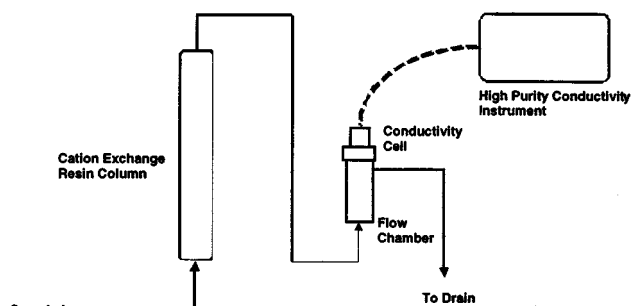


FIG. 1 Cation Conductivity Apparatus (Flow direction through the column may also be downward. See 7.1.1.)

## APPENDIX

(Nonmandatory Information)

### X1. CATION EXCHANGE COLUMN

#### X1.1 Column Diameter

X1.1.1 The flowrate and column inside diameter should provide a flow velocity of at least 300 mm/min to minimize leaching from the resin. Fig. X1.1 illustrates this relationship.

#### X1.2 Continuous Resin Rinse Scheme

X1.2.1 Lead and trail cation resin columns allow continuous rinsing of the trailing column while the lead column is "working." When the lead column is exhausted the trailing column is rinsed fully, air has been purged and it can be valved easily into the lead position with minimal interruption. The exhausted column is replaced and valved in for rinsing. Figs. X1.2-X1.4 illustrate the three modes of operation with heavy lines and shaded valve ports indicating the sample flow direction (9).

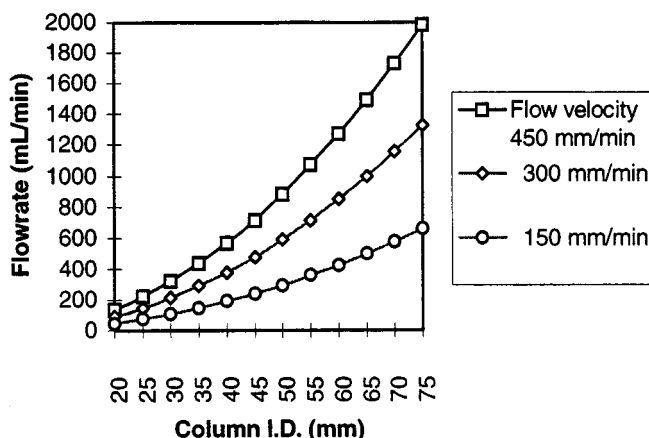


FIG. X1.1 Sample Flowrate Versus Column Inside Diameter

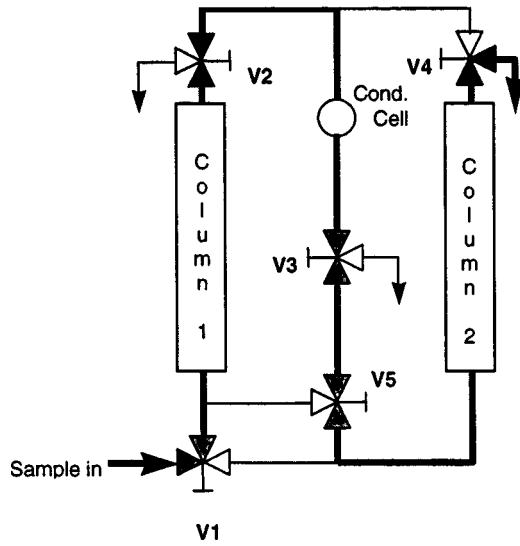


FIG. X1.2 Column 1 is exchanging cations and Column 2 is rinsing

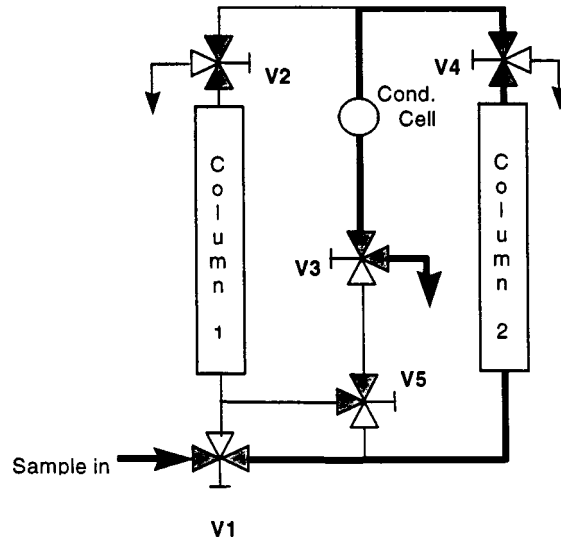


FIG. X1.3 Column 1 is exhausted and Column 2 has been valved in to exchange cations, allowing replacement of Column 1

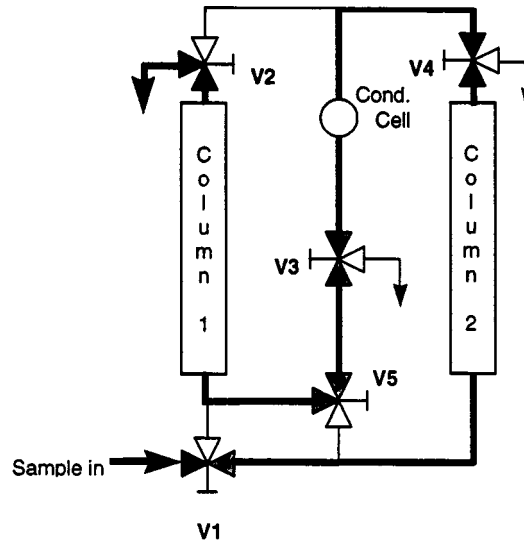


FIG. X1.4 Column 2 continues to exchange cations and a new Column 1 is rinsing

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