



Designation: ~~D5544-05~~ Designation: D5544 – 11

Standard Test Method for On-Line Measurement of Residue After Evaporation of High-Purity Water¹

This standard is issued under the fixed designation D5544; 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 determination of dissolved organic and inorganic matter and colloidal material found in high-purity water used in the semiconductor, and related industries. This material is referred to as residue after evaporation (RAE). The range of the test method is from 0.001 $\mu\text{g/L}$ (ppb) to ~~20 mg/L (ppm)~~ 60 $\mu\text{g/L}$ (ppb).

1.2 This test method uses a continuous, real time monitoring technique to measure the concentration of RAE. A pressurized sample of high-purity water is supplied to the test method's apparatus continuously through ultra-clean fittings and tubing. Contaminants from the atmosphere are therefore prevented from entering the sample. General information on the test method and a literature review on the continuous measurement of RAE has been published.²

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.* For specific hazards statements, see Section 8.

2. Referenced Documents

2.1 ASTM Standards:³

D1129 Terminology Relating to Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D3370 Practices for Sampling Water from Closed Conduits

D3864 Guide for Continual On-Line Monitoring Systems for Water Analysis

D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry

D5127 Guide for Ultra-Pure Water Used in the Electronics and Semiconductor Industries

E1184 Practice for Determination of Elements by Graphite Furnace Atomic Absorption Spectrometry

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *aerosol, n*—any solid or liquid particles, with a nominal size range from 10 nm to 100 μm , suspended in a gas (usually air).

3.2.2 *colloidal suspension, n*—any material in suspension (for example, silica) with a nominal particle size less than 100 nm.

3.2.3 *condensation particle counter (CPC)* Water-based condensation particle counter (WCPC), *n*—instrument for detecting very small aerosol particles in a size range from approximately ~~107~~ nm to 2 to 3 μm .

3.2.3.1 *Discussion*—The WCPC cannot differentiate ~~between~~ among particles of varying size within this size range; ~~it the~~ counter reports the number of particles with a size greater than that defined by its ~~the~~ detection efficiency curve. Detection is independent of particle composition.

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 of Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

Current edition approved Jan-May 1, 2005-2011. Published January 2005-May 2011. Originally approved in 1994. Last previous edition approved in 2004-2005 as D5544-94 (2004)-D5544-05. DOI: 10.1520/D5544-05; 10.1520/D5544-11.

² Blackford, D. B., and Kerrick, T. A., *Proceeding of Microcontamination '91*, San Jose, CA, 1991, pp. 39-51. Published by Canon Communications Inc., 3340 Ocean Park Blvd., Suite 1000, Santa Monica, CA 90405.

² Blackford, D. B., "Use of Nonvolatile Residue Monitoring in Semiconductor Water Applications" *Ultrapure Water Journal*, November 2008 pp 16-23 Published by Tall Oaks Publishing

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.

3.2.4 *detection efficiency, n*—in this test method, detection efficiency represents a curve relating particle size to a counter's ability to detect that size.

3.2.5 *diffusion screen, n*—a fine mesh screen used to filter residue particles of a particular size.

3.2.6 *high-purity water, n*—within the context of this test method, high-purity water is defined as water containing residue after evaporation in the range from 0.1 µg/L to 20 mg/L.

3.2.7 *polydisperse, adj*—a type of size population, in this case of aerosol particles, composed of many different sizes; the opposite of monodisperse, which is a type of size distribution of just one size.

3.2.83.2.6 *realtime, n*—the time that an event is occurring plus the response time; ~~in time.~~

3.2.6.1 *Discussion*—In this case, the response time is 3 to 5 min. ~~Therefore, min, therefore,~~ contamination is recorded 3 to 5 min after it occurs.

3.2.93.2.7 *residue after evaporation, n*—contaminants remaining after all water is evaporated; sometimes known as nonvolatile residue or total dissolved and suspended solids.

4. Summary of Test Method

4.1 This test method consists of continuously removing a representative sample of high-purity water from a pressurized supply line (refer to Practices D3370, Practice C on Continual Sampling, and Practice D3864). The temperature of the incoming high-purity water should ideally be at room temperature, but not more than 50°C. ~~The high-purity water~~ A nebulizer is subsequently cooled to a constant temperature of 18°C. ~~An atomizer is supplied with the cooled high-purity water at a constant flow rate, and a source of compressed air, or nitrogen, at a constant flow rate and pressure, to generate a stable aerosol of high-purity water droplets. Under these conditions, the atomizer~~nebulizer produces a polydisperse size distribution of droplets with a median size of approximately 1 µm, and a concentration of approximately 10⁷ droplets/s, or 10¹² droplets/mL

4.2 ~~The droplets enter a drying column; are rapidly mixed with dried, filtered, heated (normally at 120°C) compressed air, or nitrogen; and dried within the first few centimetres of the drying column. The temperature of the drying column can be set at lower temperatures (95, 70, or 45°C) if information concerning the dissolved organic fraction of residue is required. Each atomizer droplet produces a particle of nonvolatile residue. As the residue particles emerge from the drying column, a small percentage is removed and passed through a diffusion screen before being counted by a condensation particle counter (CPC). Different combinations of diffusion screens modify the detection efficiency of the CPC, allowing detection in the 0.1-µg/L to 20-mg/L range.~~

4.3 ~~The CPC works as follows: The residue particles enter a saturator and pass through a heated, volatile liquid-soaked wick. The wick dips into the liquid reservoir and continually draws up liquid through an inclined tube. The liquid evaporates and saturates the aerosol stream with vapor. *N*-butyl alcohol has been used successfully as the volatile liquid in this test method. The vapor-saturated aerosol passes into a vertical condenser tube, cooled by a thermoelectric device. The vapor cools, becomes super-saturated, and begins to condense on the particle nuclei to form large droplets that can then be counted with a relatively simple optical particle counter. A more elaborate description of the CPC's method for distinguishing between clean and dirty water is described in~~

4.2 ~~The droplets are heated at 120°C. . After the heating, additional compressed air or nitrogen is introduced from the supply to prevent re-condensation and to quickly move the residue particles to the Water-based Condensation Particle Counter (WCPC).~~

4.3 ~~The WCPC works as follows: Residue particles pass through a region called the Saturator (see Fig. 1) where the residue particles are saturated with water vapor and temperature equilibrated. The residue particles and water vapor then pass into a region called the Growth Tube, where the wetted walls of the porous media are heated to raise vapor pressure. The high diffusivity of the vapor allows it to reach the center of the sample stream at a faster rate than the thermal diffusivity of the vapor can equilibrate to the higher temperatures near the walls, resulting in a supersaturated condition along the radius of the flow stream. Residue particles in the flow stream act as nuclei for condensation. Water condenses on the residue particles to form large droplets with only one residue particle at the center of each droplet. Droplets can then be counted with a relatively simple optical particle counter. A more elaborate description of the WCPC's method for distinguishing between clean and dirty water is described in Appendix X1.~~

4.4 A calibration technique (described in detail in Section 10) uses concentration standards of high-purity potassium chloride (KCl) to convert the WCPC count concentration in particles per cubic centimetre into RAE concentration in micrograms per litre or milligrams per litre. A graphite furnace atomic absorption spectrometer (GFAAS), or equivalent method, can be used to check the concentration of KCl in this test method standard (see Practices D3919 and E1184).

5. Significance and Use

5.1 Even so-called high-purity water will contain contaminants. While not always present, these contaminants may contribute one or more of the following: dissolved active ionic substances such as calcium, magnesium, sodium, potassium, manganese, ammonium, bicarbonates, sulfates, nitrates, chloride and fluoride ions, ferric and ferrous ions, and silicates; dissolved organic substances such as pesticides, herbicides, plasticizers, styrene monomers, deionization resin material; and colloidal suspensions such as silica. While this test method facilitates the monitoring of these contaminants in high-purity water, in real time, with one instrument, this test method is not capable of identifying the various sources of residue contamination or detecting dissolved gases or suspended particles.

5.2 This test method is calibrated using weighed amounts of an artificial contaminant (potassium chloride). The density of

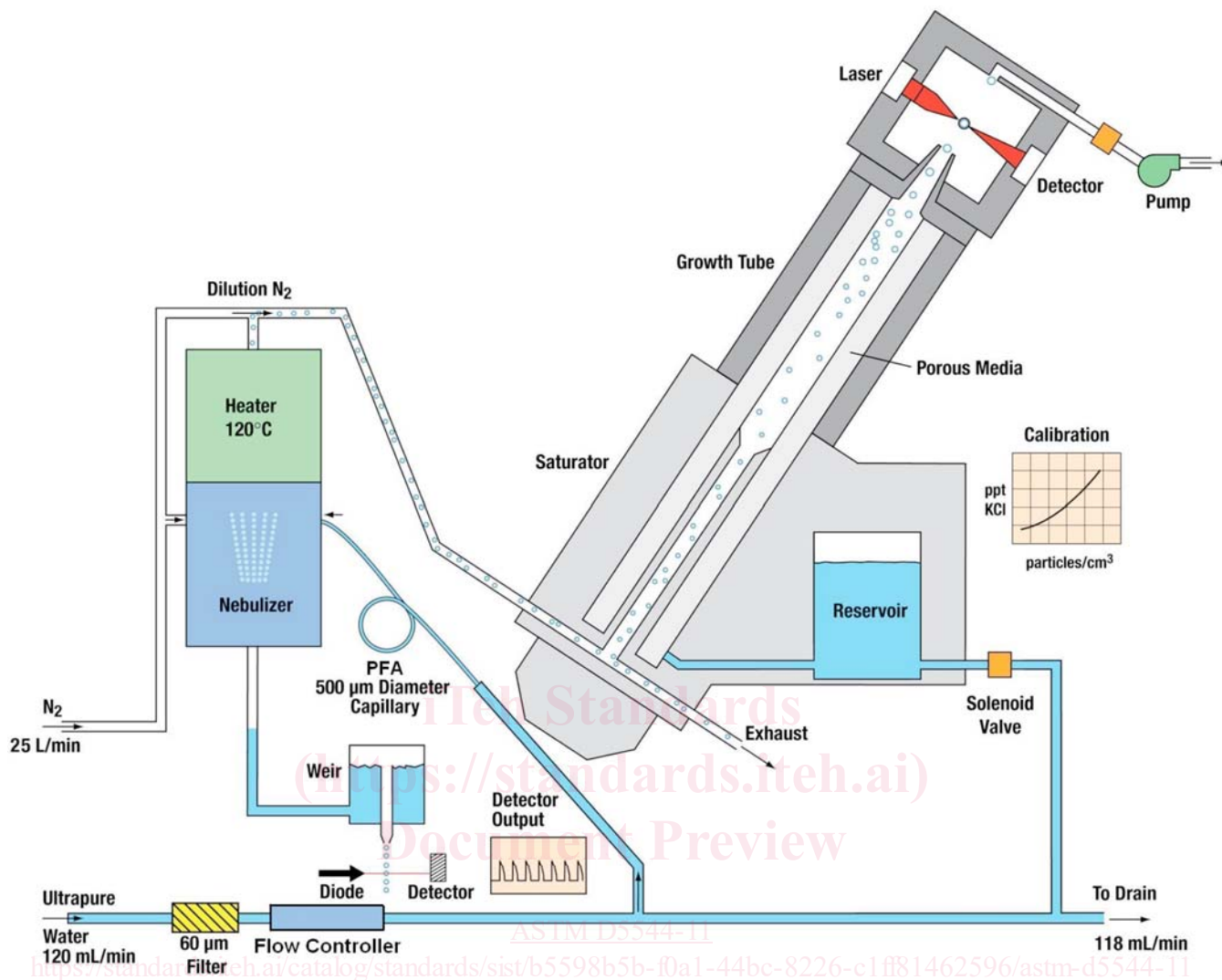


FIG. 1 Schematic Diagram of Apparatus Required for This Test Method

potassium chloride is reasonably typical of contaminants found in high-purity water; however, the response of this test method is clearly based on a response to potassium chloride. The response to actual contaminants found in high-purity water may differ from the test method's calibration. This test method is not different from many other analytical test methods in this respect.

5.3 Together with other monitoring methods, this test method is useful for diagnosing sources of RAE in ultra-pure water systems. In particular, this test method can be used to detect leakages such as colloidal silica breakthrough from the effluent of a primary anion or mixed-bed deionizer. In addition, this test method has been used to measure the rinse-up time for new liquid filters and has been adapted for batch-type sampling (this adaptation is not described in this test method).

5.4 Obtaining an immediate indication of contamination in high-purity water has significance to those industries using high-purity water for manufacturing components; production can be halted immediately to correct a contamination problem. The biomedical and power-generating industries emerging nano-particle technology industry will also benefit from this information.

6. Apparatus

6.1 The schematic arrangement of the system is shown in Fig. 1. The apparatus is available as a complete instrument⁴.

6.2 *Flow Controller*, made of a non-contaminating material such as perfluoroalkoxy (PFA), necessary to supply the atomizer with high-purity water at the desired flow rate. The flow controller must contain a pressure regulator to ensure that water is delivered to the atomizer at a stable flow rate, despite external fluctuations. High-purity water must be delivered to the flow controller and atomizer through ultra-clean tubes and fittings made from PFA polytetrafluoroethylene. Atomizers usually require a very low flow

⁴ The sole source of supply of the apparatus known to the committee at this time is Fluid Measurement Technologies, 4225-4106 Hoffman Road, White Bear Parkway, Suite 1225, Vadnais Heights, Lake, MN 55110. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

rate, approximately 1 mL/min, for efficient operation. However, such a low flow rate is inadequate for routine monitoring because it results in a long response time. This test method is designed to overcome the problem of long response times by using a flow controller to deliver approximately 70 mL/min of high-purity water to the monitoring site and then to divert 1 mL/min of the flow to the atomizer through a short tube. This short tube facilitates a short response time.

6.2 2 60 μ m Filter, high purity water flows into the apparatus at approximately 120 mL/min and immediately passes through a 60 μ m sintered stainless filter that removes any large debris and then flows to flow controller.

6.3 *Cooling Block*, necessary to cool the water and maintain it at a stable temperature before it enters the atomizer (18°C is adequate). The cooling block incorporates a thermoelectric device capable of maintaining the cooling block at the required temperature. Flow Controller, made of a non-contaminating material such as perfluoroalkoxy (PFA), necessary to supply the nebulizer with high-purity water at the desired flow rate. The flow controller must contain an air actuated pressure regulator to ensure that water is delivered to the nebulizer at a stable flow rate, despite external fluctuations. High-purity water must be delivered to the flow controller and nebulizer through ultra-clean tubes and fittings made from PFA. Nebulizers usually require a very low flow rate, approximately 1 mL/min, for efficient operation. However, such a low flow rate is inadequate for routine monitoring because it results in a long response time. This test method is designed to overcome the problem of long response times by using a flow controller to deliver approximately 120 mL/min of high-purity water to the monitoring site and then to divert approximately 1 mL/min of the flow to the nebulizer through a short tube. This short tube facilitates a short response time. From the pressure regulator, the water flows to the nebulizer through a tee fitting and a section of PFA 500 μ m capillary tubing. The PFA tubing gradually lowers the water pressure and prevents any out-gassing of dissolved gases in the incoming water.

6.4 *Atomizer* Measuring the Flow Rate, the flow rate of water flowing through the nebulizer is used as an indicator that the NRM 8000 is set up and operating correctly. Instead of using a conventional flow meter, the NRM 8000 incorporates a new, patented method of measuring the flow rate. Of the water flowing through the nebulizer, 95% leaves it as part of a waste stream. The waste water is collected by a weir and stand-pipe system and then delivered as a steady stream of water droplets of identical size. These droplets fall through a simple light beam. As each droplet breaks the beam, a detector senses a scattered light signal, or pulse, and a counter keeps track of the pulses. An algorithm converts the pulse count to a flowrate (in mL/min.) which is shown on the front panel display.

6.5 *Nebulizer*, required to produce a polydisperse size distribution of droplets with a median size of approximately 1 μ m and a concentration of approximately 10^7 droplets/s. The atomizer must be supplied with clean, dried filtered compressed air or nitrogen and must be machined from a material that will not contaminate the high-purity water. Passivated 316 stainless steel has been used successfully in this test method. Details of how to passivate stainless steel can be found in the *droplets/s. Within the customized designed nebulizer, the water and compressed air/nitrogen (supplied at a constant flow rate and pressure) combine to form the required stable, poly-dispersed aerosol of ultrapure water droplets. The nebulizer must be supplied with clean, dried filtered compressed air or nitrogen and must be machined from a material that will not contaminate the high-purity water. Passivated 316L stainless steel has been used successfully in this test method. Details of how to passivate stainless steel can be found in the Metal Finishing Guidebook.*⁵

6.5 *Mixing Chamber and Drying Column*, for mixing the water droplets from the atomizer with dried, heated (at 120°C or, if required, 95, 70, or 45°C) dilution air or nitrogen. The water droplets and dilution air pass through a drying column that evaporates all of the water from the droplets. The residue from each droplet is left as a particle. A drying column approximately 2.5 cm in diameter and 30 cm in length has worked well in this test method, with a ratio of dilution air to atomizer air of approximately 10:1.

6.6 *Diffusion Screens*—Fifty-millimetre diameter diffusion screens made of a fine stainless steel wire cloth used to shift the detection efficiency of the CPC to larger sizes. Wire cloth with a wire diameter of 25 μ m and a square weave opening of 38 μ m (referred to as a 400 mesh in the Tyler equivalent designation) has worked well in this test method. Heater and Dilution air/nitrogen, the ultrapure water droplets produced by the nebulizer are rapidly heated at 120°C. Each water droplet is evaporated to dryness, leaving behind a particle of residue consisting of dissolved inorganic material. Every nebulizer droplet results in a residue particle: the cleaner the ultrapure water, the smaller the amount of residue within each droplet, and the smaller the resulting residue particle. After the heating, additional compressed air or nitrogen, is introduced from the supply to prevent re-condensation and to quickly move the residue particles to the Water-based Condensation Particle Counter (WCPC).

6.7 *Condensation Particle Counter*(CPC), containing a saturator, condenser, and optical particle counter to enlarge the particles to a uniform size and count them in particles per cubic centimetre. The flow rate through the CPC is 2.8 L/min:

6.7.1 Inside the saturator is a wick soaked in a volatile liquid. The wick dips into a liquid reservoir and draws up liquid continually through an inclined tube. The liquid evaporates and saturates the aerosol stream with vapor.

6.7.2 The vapor-saturated aerosol passes into a vertical condenser tube, cooled by a thermoelectric device. Aerosol particles of a certain size and above (nominally 10-nm diameter) act as nucleation sites upon which the vapor can condense to form droplets (nominally 10- μ m diameter). Droplets pass from the condenser tube through a nozzle into the optical detector.

6.7.3 The CPC's focusing optics consist of a laser diode and beam-shaping optics. This combination forms a beam of laser light above the aerosol exit nozzle. The sensor's collecting optics collect the light scattered by the droplets and focus this light onto a low-noise photo-detector. Water-based Condensation Particle Counter (WCPC), The WCPC uses a patented technology to count

⁵ *Metal Finishing Guidebook*, Elsevier Science, New York, NY, 60th ed., 1992.

residue particles. Water is used as the working fluid and mixing or adiabatic expansion techniques are not needed. A condensation nucleation technique deposits water on the residue particles to grow them to a size that can be detected with a conventional optical counting system. The stream of residue particles is uninterrupted and follows a laminar flow path from the sample inlet to the optical detector. The WCPC particle counting process is as follows:

- (1) The residue particles are mixed with water vapor in the Saturator and then temperature equilibrated.
- (2) The residue particles pass to a growth tube where the wetted walls (composed of a porous ceramic medium) are heated to raise the vapor pressure. The high diffusivity of the water vapor allows the vapor to reach the center of the sample stream at a faster rate than the thermal diffusivity of the vapor can equilibrate to the higher temperatures near the walls – creating a supersaturated condition along the radius of the flow stream. These unstable conditions facilitate water condensation on the residue particles.
- (3) The residue particles that are larger than the detection limit of the WCPC particle critical size act as condensation nuclei as they pass up the growth tube.
- (4) The enlarged particles are detected by the optical detector.
- (5) The WCPC's focusing optics consist of a laser diode and beam-shaping optics. This combination forms a beam of laser light above the aerosol exit nozzle. The sensor's collecting optics collect the light scattered by the droplets and focus this light onto a low-noise photo-detector.

7. Reagents and Materials

7.1 *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. 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 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean Electronic and Semiconductor grade water Type E1, E1.1, or E1.2 of Specification D5127.

7.3

7.2 *Potassium Chloride (KCl) as a Dry Powder*—KCl purity should be >99.98 %.^{4,6} Weighed amounts of KCl, in dry form, are dissolved in water to generate calibration solutions of known concentration. See 10.2 and 10.2.1 for preparing these calibration solutions. The solutions must be prepared carefully under clean laboratory conditions. Use clean 250-mL PFA beakers and a microbalance capable of measuring to 0.01 mg.

7.4 *Volatile Liquid*—This test method uses a volatile liquid in the CPC for the particle enlarging process. An alcohol such as *n*-butyl alcohol is a suitable liquid.

8. Hazards

8.1 **Warning:** The instrument used in this test method incorporates a Class I laser. There is no danger under normal installation and operation conditions. However, if instructions are not followed carefully, the operator can be subjected to hazardous radiation in the form of intense, focused, invisible light.

8.2 **Warning:** The instrument used in this test method is designed to analyze high-purity water. Flammable solvents, such as alcohol and acetone, cannot be analyzed in this test method.

8.3 **Warning:** The instrument used in this test method is designed to use a volatile liquid during its operation. The instrument should be used only in a well-ventilated area.

9. Sampling Requirements

9.1 High-purity water must be supplied through ultra-clean fittings made of a material that will not contaminate the water. Perfluoroalkoxy (PFA) has been used successfully with this test method. PFA is a fully fluorinated, translucent polymer of exceptional purity. It does not release a gas and is resistant to virtually all chemicals and solvents.

9.2 High-purity water should not be exposed to the atmosphere because it picks up contamination readily. This test method requires a continuous flow of high-purity water through a sealed, on-line installation to prevent such contamination.

9.3 This test method requires a non-contaminating pressure regulator because high-purity water must be supplied to the atomizernebulizer at a constant flow rate. Pressure fluctuations in the high-purity water supply must not be allowed to affect the flow rate of water supplied to the atomizernebulizer because pressure fluctuations will affect the size of water droplets produced by the atomizernebulizer, making the calibration inaccurate.

9.4 The atomizernebulizer requires a source of high-pressure compressed air, or nitrogen, regulated at a constant pressure to generate a stable aerosol of high-purity water droplets with a median size of approximately 1µm.

9.5 Water entering the atomizer must be at a temperature of 18±1°C, to control surface tension in the high-purity water. Changes in surface tension affect the size distribution of water droplets.

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 Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁶ The sole source of supply of KCl known to the committee at this time is Aldrich Chemical Co., Inc., 1001 West St. Paul Ave., Milwaukee, WI 55233.

9.6 Using long sample lines with low sample velocity to divert the flow of high-purity water to the test apparatus is not recommended, as this allows contaminants to accumulate in the sample lines. Sample lines should therefore be less than 2 m long, and line velocity should be greater than 10 cm/s. If the instrumentation for this test method cannot be sited close to the high-purity water supply, a sample line with a velocity of at least 1.8 m/s should bring the high-purity water to a tee connection. One of the branches of the tee should provide high-purity water to the instrumentation for this test method, and the other branch should go to drain.

10. Calibration and Standardization

10.1 The WCPC measures particle concentration in units of particles per cubic centimetre. This test method incorporates a calibration technique to equate the WCPC's measurement in particles per cubic centimetre with RAE concentration in micrograms per litre or milligrams per litre. The calibration technique requires a motorized syringe injector to introduce a controlled amount of impurity into the water being tested, KCl to perform the calibration procedure, and a micro-balance to weigh KCl for a standard concentration for injection. A GFAAS, or equivalent method, checks the KCl concentration.

10.1.1 Fig. 2 is an illustration of the apparatus used in the specified calibration procedure. Fig. 3 is an illustration of the method of withdrawing a sample for GFAAS analysis, or equivalent method.

10.1.2 The motorized syringe injects a controlled amount of impurity into the high-purity water being monitored. The impurity is injected at a constant rate directly into a sample introduction tee with a septum. The septum allows the sample to be injected without interrupting the flow of water to the instrument. To perform the calibration successfully requires a clean syringe large enough to allow several hours of uninterrupted operation; a 60-mL polypropylene syringe is recommended. A mixing valve should be installed after the introduction tee to mix the injected impurity with the high-purity water sample. A partially open stopcock works well as a mixing valve.

10.1.3A GFAAS complying to Practice

10.1.3 A GFAAS, or equivalent method, complying to Practice E1184 and capable of determining potassium in accordance with Practice D3919 is required. In this test method, the GFAAS, or equivalent method, is used to measure the potassium (K) atoms present in the KCl calibration solutions. When the amount of K present is determined, the amount of KCl in the calibration solution can be calculated.

10.2 Calculate the amount of KCl to use in a particular solution with the following formula:

$$K = \frac{VFC}{SA (10^6)} \tag{1}$$

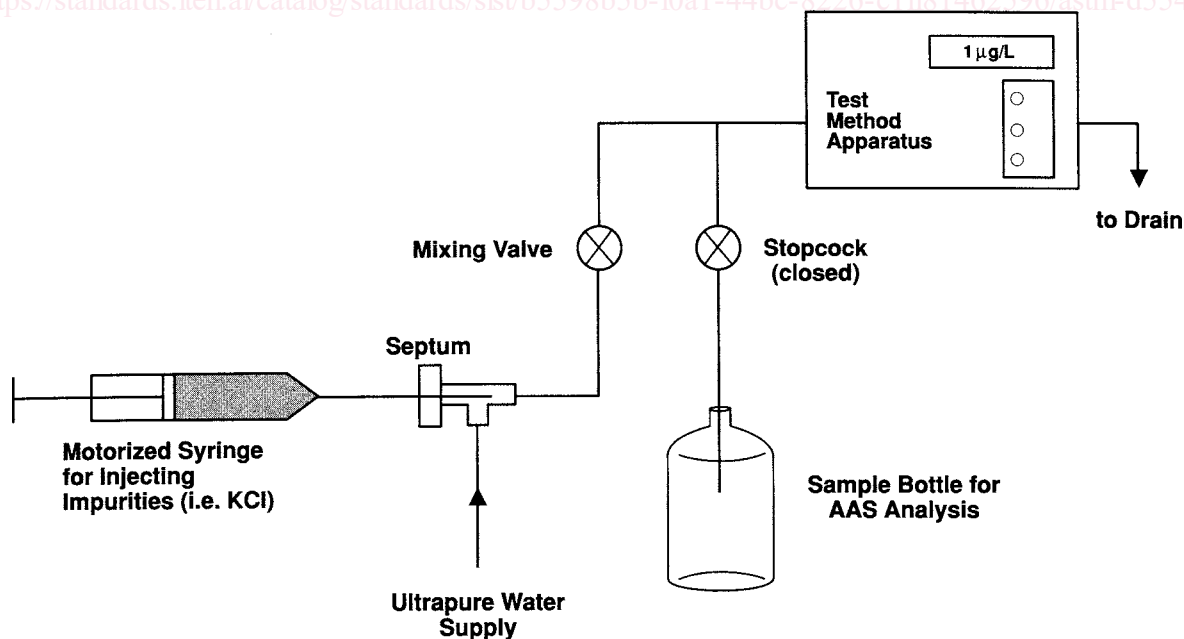


FIG. 2 Schematic Diagram of Calibration Apparatus