Standard Test Method for On-Line Measurement of Residue After Evaporation of High-Purity Water[1]

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 µg/L (ppb) to 60 µg/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 standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

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 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 *Water-based condensation particle counter (WCPC), n*—instrument for detecting very small aerosol particles in a size range from approximately 7 nm to 2 to 3 µm.

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

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 *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.

3.2.6 *realtime, n*—the time that an event is occurring plus the response time.

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[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] Blackford, D. B., "Use of Nonvolatile Residue Monitoring in Semiconductor Water Applications" *Ultrapure Water Journal*, Tall Oaks Publishing, November 2008, pp. 16–23.

[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.

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

3.2.7 *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. A nebulizer is supplied with the 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 nebulizer produces a polydisperse size distribution of droplets with a median size of approximately 1 µm, and a concentration of approximately 10^7 droplets/s, or 10^{12} droplets/mL

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

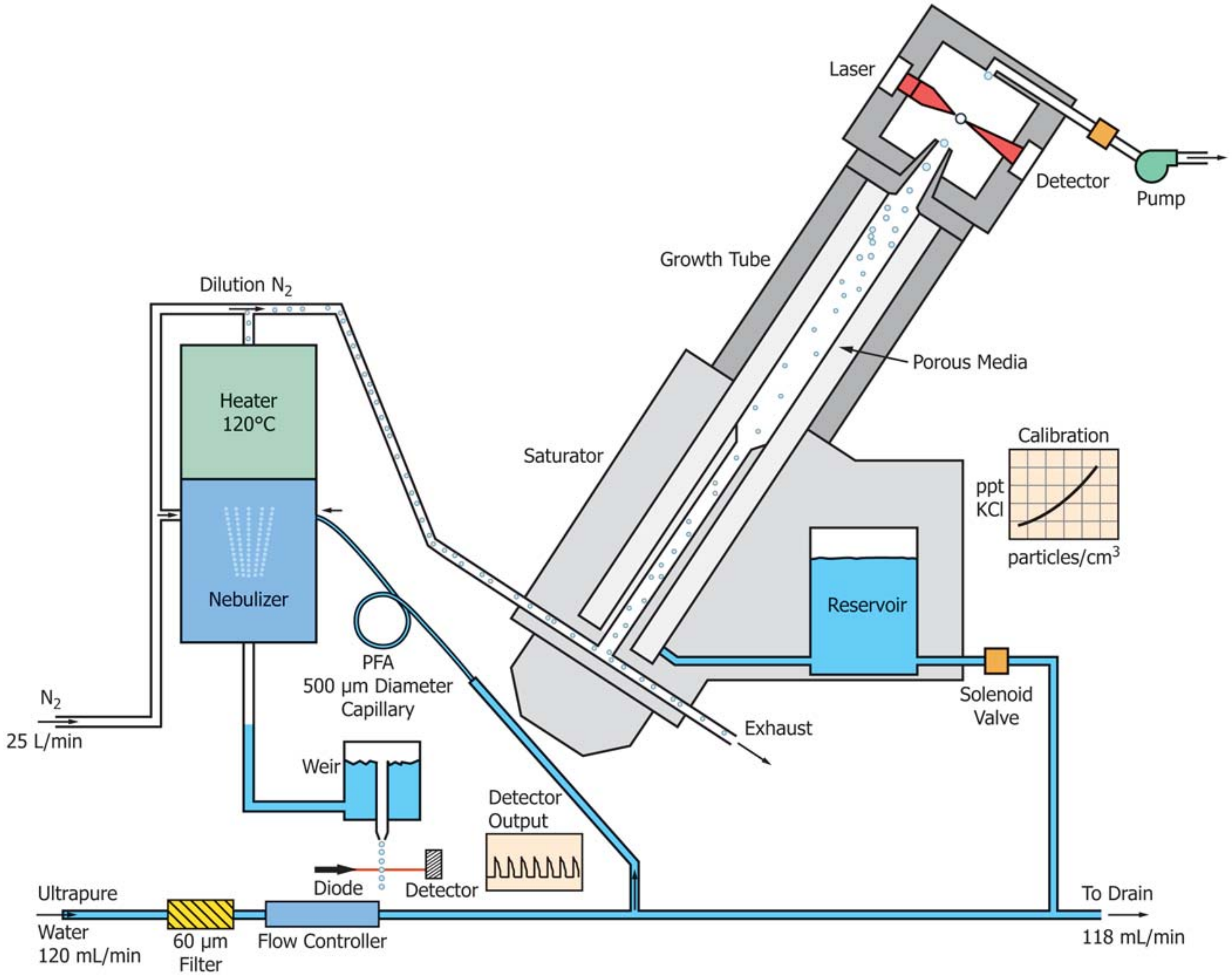

FIG. 1 Schematic Diagram of Apparatus Required for This Test Method

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 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 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 instrument.[4]

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

6.3 *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 500µm capillary tubing. The PFA tubing gradually lowers the water pressure and prevents any outgassing of dissolved gases in the incoming water.

6.4 *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 µm and a concentration of approximately 10^7 droplets/s. Within the customed 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

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[4] The sole source of supply of the apparatus known to the committee at this time is Fluid Measurement Technologies, 4106 Hoffman Road, White Bear 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 [1], which you may attend.

used successfully in this test method. Details of how to passivate stainless steel can be found in the *Metal Finishing Guidebook.*[5]

6.6 *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 *Water-based Condensation Particle Counter (WCPC),* the WCPC uses a patented technology to count 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 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.

7.2 *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.

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.

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 nebulizer 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 nebulizer because pressure fluctuations will affect the size of water droplets produced by the nebulizer, making the calibration inaccurate.

9.4 The nebulizer 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 1 μm.

9.5 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

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

[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. 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 [1], which you may attend.

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.

10.1.3 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:

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

where:

K = weight of KCl, mg,
V = volume of Type I reagent water, mL,
F = high-purity water flow rate through instrument, mL/min,
C = desired concentration, µg/L,
S = syringe injection speed, cm/min, and
A = syringe cross-sectional area, cm^2.

10.2.1 *Example*—To determine how much KCl to dissolve in 100 mL of Type I reagent water ($V = 100$) if the desired concentration is 100 µ/L, µg/L, ($C = 100$), the motorized syringe drive is set to push the plunger into the syringe at a rate of 5×10^{-4} cm/s ($S = (5 \times 10^{-4}) \times 60$ cm/min), the 60-mL syringe has a cross-sectional area of 5.07 cm^2 ($A = 5.07$ cm^2), and the high-purity water flow rate through the instrument is 70 mL/min ($F = 70$):

$$K = \frac{(100)(70)(100)}{(5 \times 10^{-4})(60)(5.07)(10^{6})} = 4.60 \text{ mg} \tag{2}$$

To produce the calibration solution described in this example, one must dissolve 4.60 mg of KCl in 100 mL of Type I reagent water. To inject this solution, fill the 60-mL syringe

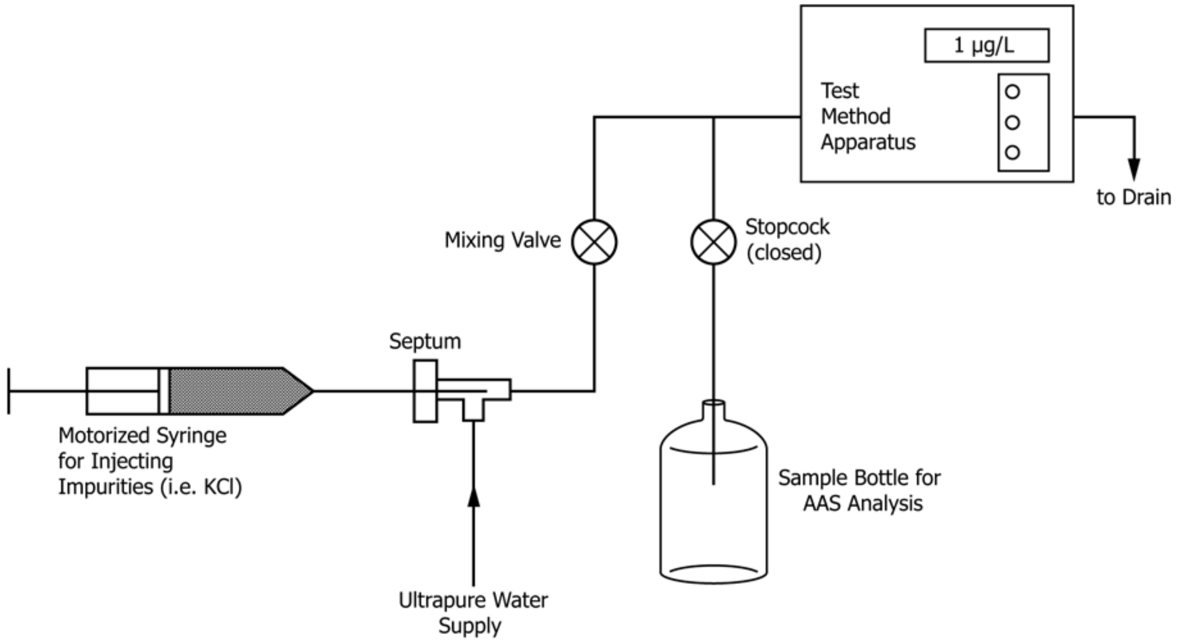

FIG. 2 Schematic Diagram of Calibration Apparatus

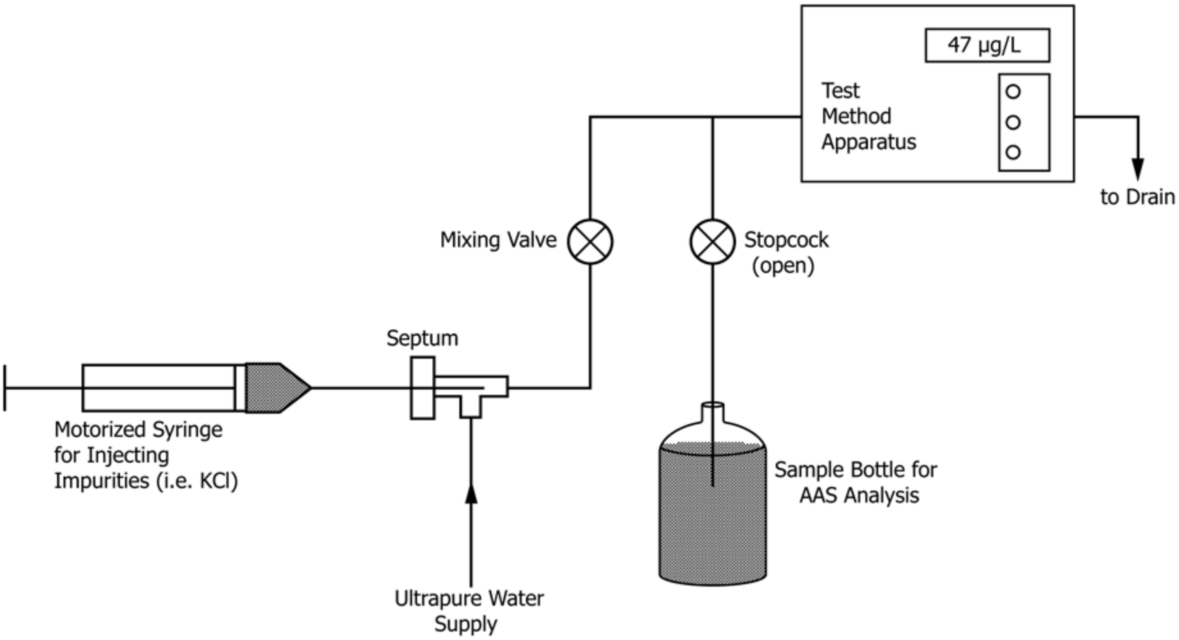

FIG. 3 Illustration of Procedure for Withdrawing a Sample for GFAAS Analysis

and set the syringe feed rate at 5 × 10^{-4} cm/s and ensure that 70 mL/min of high-purity water is flowing through the instrument. The apparatus will show a reading of 100 µg/L.

10.3 Prepare a calibration curve as follows:

10.3.1 Calculate the amount of KCl injected in accordance with 10.2.

10.3.2 Record the WCPC concentration (in particles per cubic centimetre) when the contamination level has stabilized.

10.3.3 Open the stopcock and remove a 50-mL sample, in a clean PFA or polypropylene beaker, for GFAAS analysis, or equivalent method (see Fig. 3).

10.3.4 Plot a calibration point using the calculated amount of KCl and the WCPC concentration. For KCl concentrations >2 µg/L, compare the calculated concentration to that measured by the GFAAS, or equivalent method. The calibration point is accepted if the two values are within ±5 %; if not, the calibration point must be repeated.

10.3.5 Repeat this procedure to find a total of ten calibration points.

10.3.6 Plot the points on a log-log scale of micrograms per litre of KCl versus WCPC particles per cubic centimetre and draw a calibration curve.

10.3.7 Alternatively load the calibration data into the WCPC's internal memory. The calibration procedure is now completed.

10.4 A typical calibration curve is shown in Fig. 4. The calibration procedure must be performed every 12 months.

11. Procedure

11.1 Site the testing apparatus near the source of the high-purity water to be monitored for contamination.

11.2 Supply the atomizer with filtered, dried, oil-free air, or nitrogen regulated at approximately 349 kPa (50 psi). Connect the water supply to the flow controller, and then allow high-purity water to flow through the supply lines and the atomizer for a sufficient length of time to flush any standing contaminants out of the system. This procedure could take as long as several days if the tubes, fittings, and atomizer are dirty; it will take at least 2 h once the supply is connected.

11.3 When the system has been flushed, contamination monitoring begins. This test method has a very short response time (approximately 2 minutes) before accurate readings of RAE in the sample are displayed.

11.4 Fig. 1 illustrates the path the high-purity water takes through the monitoring system described by this test method. When all elements of the system are in place, there is little for the operator to do except to routinely check the digital flow rate measurement of water flowing through the nebulizer.

11.5 After the calibration curve is applied, the results are reported as RAE in nanograms per litre.

12. Precision and Bias

12.1 Neither precision nor bias data can be obtained for this test method from a collaborative study designed in accordance with the requirements of Practice D2777 since this test method is a continuous determination. This inability of Practice D2777 procedures to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D2777.

12.2 To provide users with a demonstration of capability of this test method's measurement of RAE, the following experiment was performed. A constant source of KCl contaminant was injected into a continuous water supply with the custom-built motorized syringe injection system shown in Fig. 2. This constant injection of a calculated amount of 130 ng/L of KCl was monitored by this test method's apparatus for an injection time of 2 hours. The results of this experiment are shown in

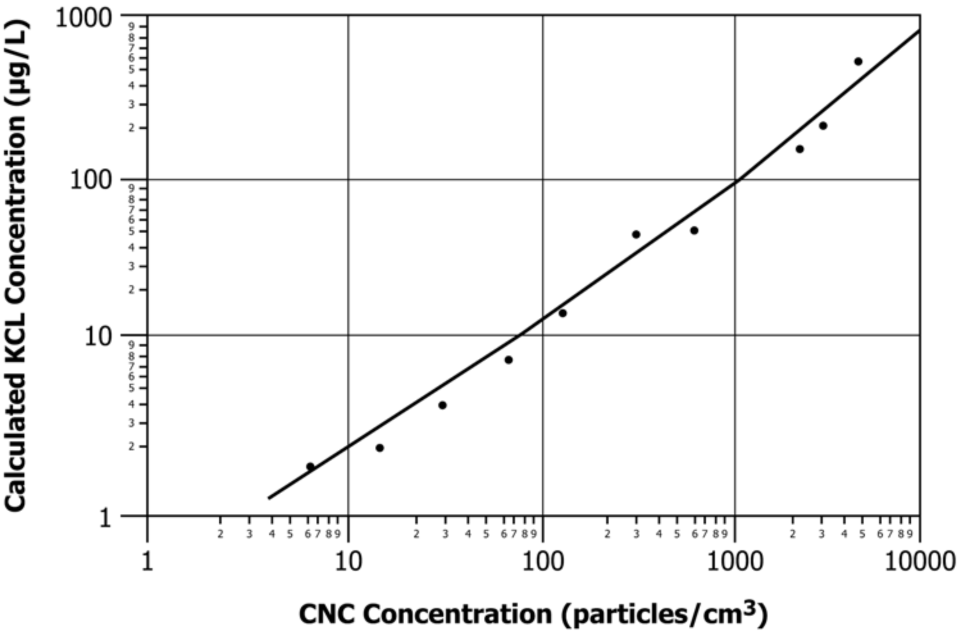

FIG. 4 A Typical Calibration Curve

Fig. 5. The median value of the data is 229 ng/L, with a standard deviation of 12.02 ng/L.

12.3 The graph shows a KCl challenge of 130 ppt (ng/L) for a period of 120 minutes, with a before and after background of approximately 100 ppt (ng/L). During the challenge the median value was calculated to be 229 ppt (ng/L), with a standard deviation of 12.02 ppt (ng/L).

13. Quality Control

13.1 An annual calibration of the measurement technique described in this test method has been found to be adequate. A sequential challenge of eight levels of KCl varying from 50 ng/L to 60 ug/L can be accomplished in about 4 hours. A new calibration curve can be fitted to this data and data form this calibration curve can be entered into memory. Experience has shown that the calibration drifts less than 5 % after 12 months of continual use.

14. Keywords

14.1 high-purity water; nonvolatile residue; residue after evaporation

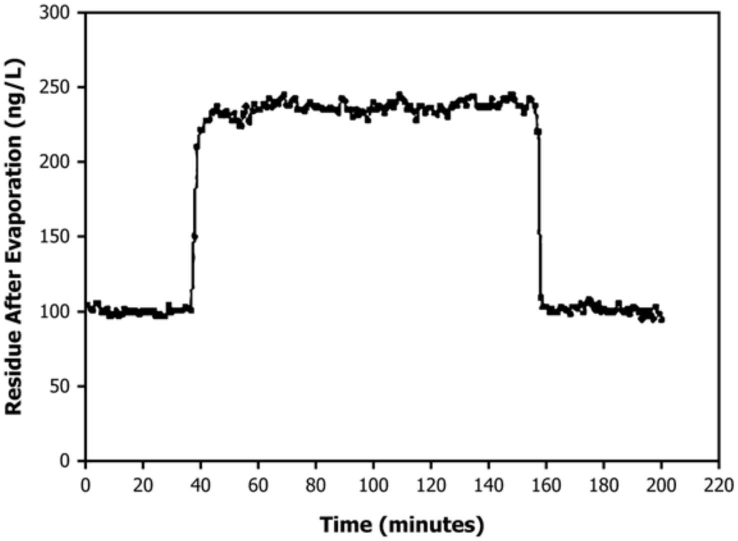

FIG. 5 Precision and bias data for the new version of the NRM

APPENDIX

(Nonmandatory Information)

X1. DISTINGUISHING BETWEEN CLEAN AND DIRTY WATER WITH A CONDENSATION PARTICLE COUNTER (WCPC)

X1.1 Like all other particle counters, the WCPC has its lower detection efficiency defined by a curve ranging from 0 % efficiency at some size to 100 % efficiency at a larger size. In this test method, the nebulizer produces a Gaussian size distribution of nonvolatile residue particles. Fig. X1.1 shows a possible size distribution of residue particles superimposed on top of the detection efficiency curve of the WCPC. Particles to the left of the efficiency curve do not initiate nucleation and are therefore not counted. Particles to the right of the efficiency curve act as sites for nucleation and are counted.

X1.2 If the high-purity water suddenly becomes dirtier such as would happen after the introduction of a contaminant, the situation illustrated in Fig. X1.2 occurs. Each droplet from the nebulizer is still approximately the same size but contains more residue. When the high-purity water droplet dries, the resulting particle is larger, and the Gaussian size of the residue particles shift to the right when superimposed on top of the WCPC's detection efficiency curve. As the high-purity water becomes dirtier, the number of residue particles able to initiate nucleation increases and the WCPC counts more particles.

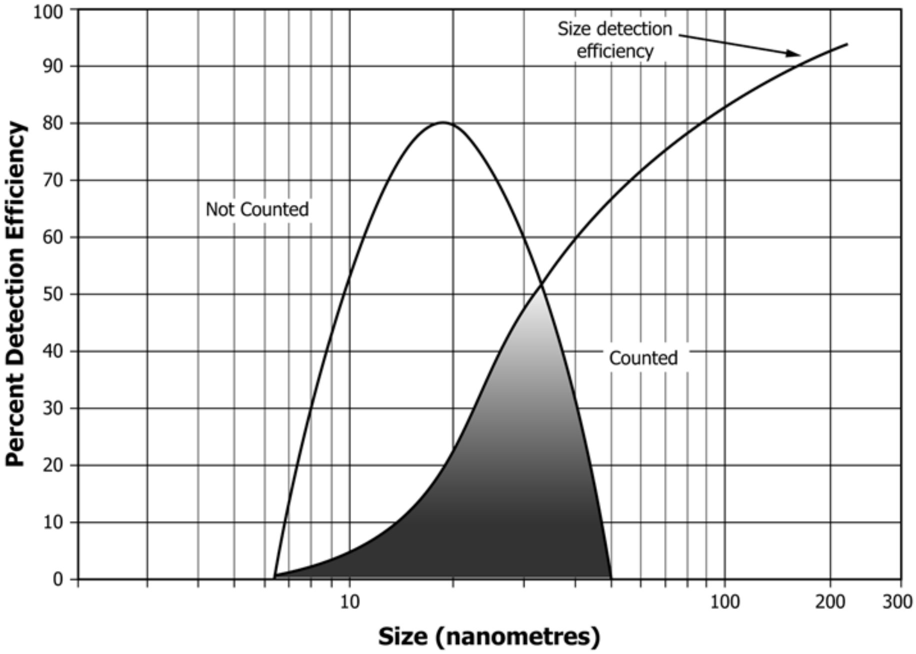

FIG. X1.1 Size Distribution of Residue from Clean Water

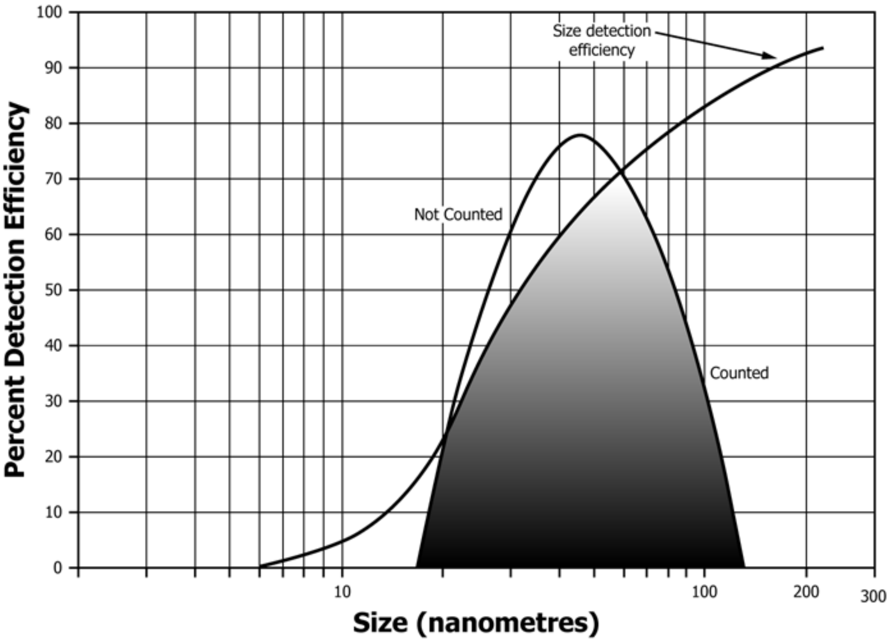

FIG. X1.2 Size Distribution of Residue from Dirty Water

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