Designation: D 5544 – 94 (Reapproved 1999)$^{\epsilon 1}$

An American National Standard

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

This standard is issued under the fixed designation D 5544; 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.

ϵ^1 NOTE—Footnotes were editorially removed in June 1999.

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, aerospace, and other industries. This material is referred to as residue after evaporation (RAE). The range of the test method is from 0.1 µg/L(ppb) to 20 mg/L (ppm).

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:*

D 1129 Terminology Relating to Water[3]
D 1193 Specification for Reagent Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[3]
D 3370 Practices for Sampling Water from Closed Conduits[3]
D 3864 Practice for Continual On-line Monitoring Systems for Water Analysis[3]
D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry[3]
E 1184 Practice for Electrothermal (Graphite Furnace) Atomic Absorption Analysis[4]

3. Terminology

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

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 nucleus counter (CNC)*, *n*—instrument for detecting very small aerosol particles in a size range from approximately 10 nm to 2 to 3 µm. The CNC cannot differentiate between particles of varying size within this size range; it reports the number of particles with a size greater than that defined by its 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 *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 size population, in this case of aerosol particles, composed of many different sizes; the opposite of monodisperse, a distribution of just one size.

3.2.8 *realtime*, *n*—the time that an event is occurring plus the response time; in this case, the response time is 3 to 5 min. Therefore, contamination is recorded 3 to 5 min after it occurs.

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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 of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water.

Current edition approved Sept. 15, 1994. Published November 1994.

[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.

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

[4] *Annual Book of ASTM Standards*, Vol 03.06.

3.2.9 *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 D 3370, Practice C on Continual Sampling, and Practice D 3864). The temperature of the incoming high-purity water should ideally be at room temperature, but not more than 50°C. The high-purity water 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 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 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 nucleus counter (CNC). Different combinations of diffusion screens modify the detection efficiency of the CNC, allowing detection in the 0.1-µg/L to 20-mg/L range.

4.3 The CNC 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 CNC'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 CNC 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) can be used to check the concentration of KCl in this test method standard (see Practices D 3919 and E 1184).

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 biomedical and power-generating industries 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,[5] or the individual components[6] described in 6.4, 6.6, and 6.7 can be purchased separately.

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 polytetrafluor-oethylene. Atomizers 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 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.

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[5] Available from TSI Inc., P.O. Box 64394, St. Paul, MN 55164.

[6] Available from Particle Measuring Systems, 5475 Airport Blvd., Boulder, CO 80301.

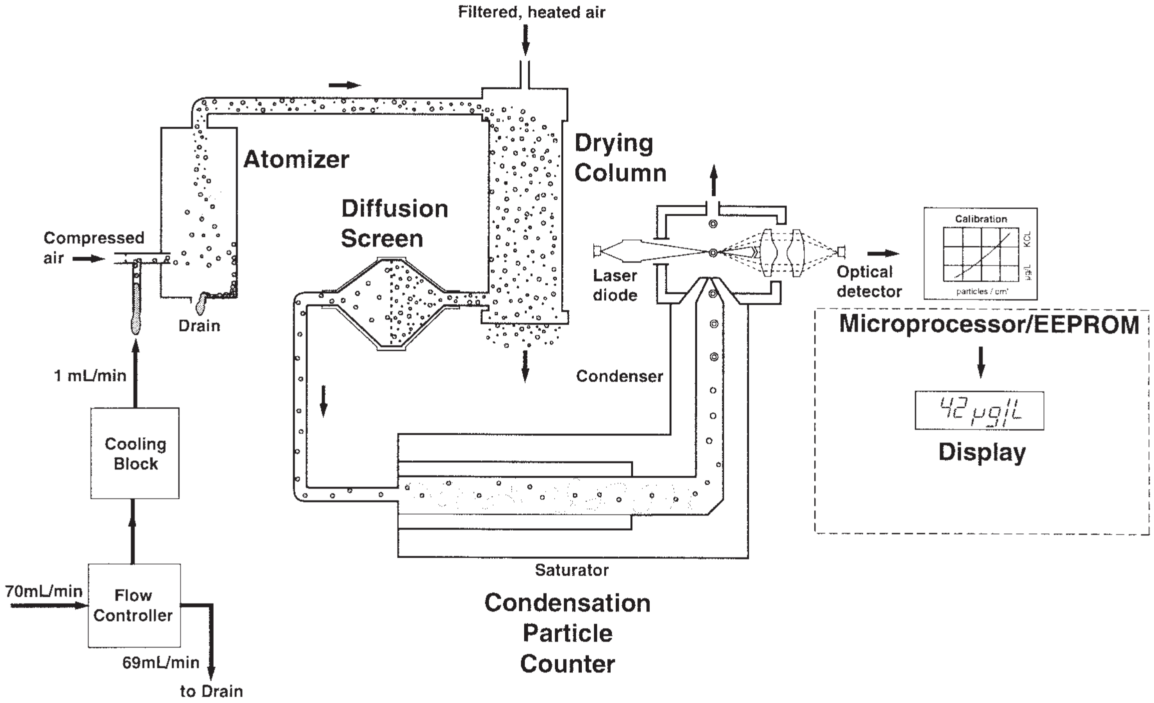

FIG. 1 Schematic Diagram of Apparatus Required for This Test Method

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.

6.4 *Atomizer*, 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. 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 *Metal Finishing Guidebook.*[7]

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 CNC to larger sizes. Wire cloth with a wire diameter of 25 µm and a square weave opening of 38 µm (referred to as a 400 mesh in the Tyler equivalent designation) has worked well in this test method.

6.7 *Condensation Nucleus Counter* (CNC), 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 CNC 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-µm diameter). Droplets pass from the condenser tube through a nozzle into the optical detector.

6.7.3 The CNC'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

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

such specifications are available.[8] 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 reagent water as defined by Type I of Specification D 1193.

7.3 *Potassium Chloride* (KCl) *as a Dry Powder*—KCl purity should be >99.98 %.[9] 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 CNC 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 atomizer 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 atomizer because pressure fluctuations will affect the size of water droplets produced by the atomizer, making the calibration inaccurate.

9.4 The atomizer 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 1μ m.

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.

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 CNC measures particle concentration in units of particles per cubic centimetre. This test method incorporates a calibration technique to equate the CNC'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 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.

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 complying to Practice E 1184 and capable of determining potassium in accordance with Practice D 3919 is required. In this test method, the GFAAS 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:

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

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[8] *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.

[9] KCl from Aldrich Chemical Co., Inc., 1001 West St. Paul Ave., Milwaukee, WI 55233, has been found suitable. Other sources may be available.

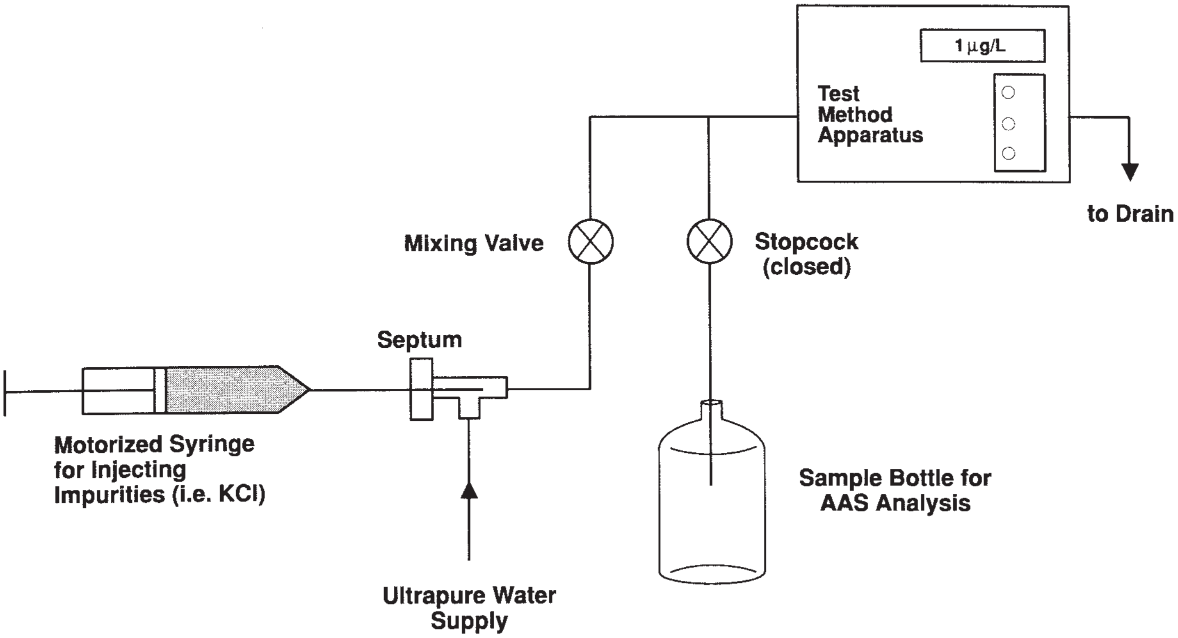

FIG. 2 Schematic Diagram of Calibration Apparatus

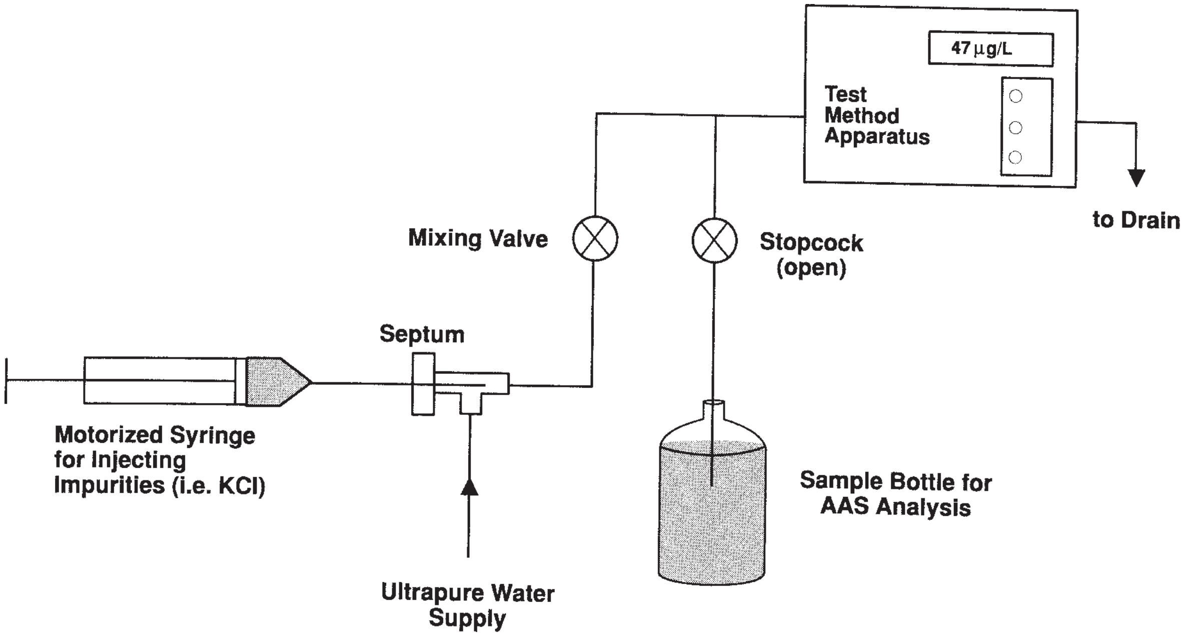

FIG. 3 Illustration of Procedure for Withdrawing a Sample for GFAAS Analysis

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 ($F = 70$):

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

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 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 CNC 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 (see Fig. 3).

10.3.4 Plot a calibration point using the calculated amount of KCl and the CNC concentration. For KCl concentrations >2 µg/L, compare the calculated concentration to that measured by the GFAAS. 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 CNC particles per cubic centimetre and draw a calibration curve.

10.3.7 Alternatively load the calibration data into the CNC'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 4 min) 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 level of the volatile liquid in the CNC's reservoir and the various water and air pressures. The reservoir containing the volatile liquid will require filling every two to three weeks.

11.5 After the calibration curve is applied, the results are reported as RAE in micrograms 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 D 2777 since this test method is a continuous determination. This inability of Practice D 2777 procedures to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D 2777.

12.2 To provide users with information on the stability 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

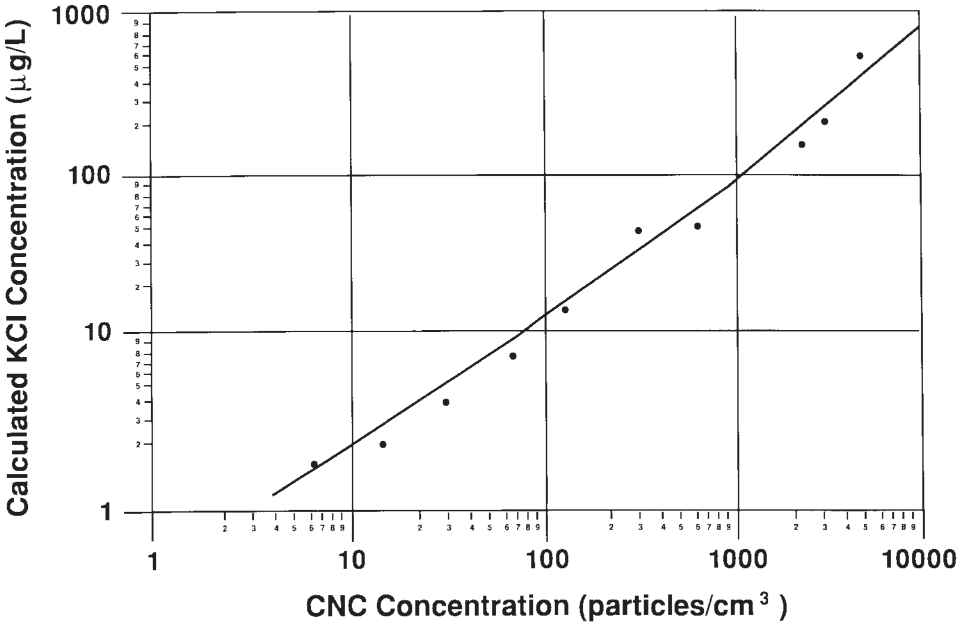

FIG. 4 A Typical Calibration Curve

constant injection of KCl was monitored by this test method's apparatus until the syringe emptied; total injection time was 4 h. The results of this experiment are shown in Fig. 5. The median value for this data is 50 µg/L, with a maximum value of 53 µg/L and a minimum value of 48 µg/L. The standard deviation was 0.807 µg/L.

13. Keywords

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

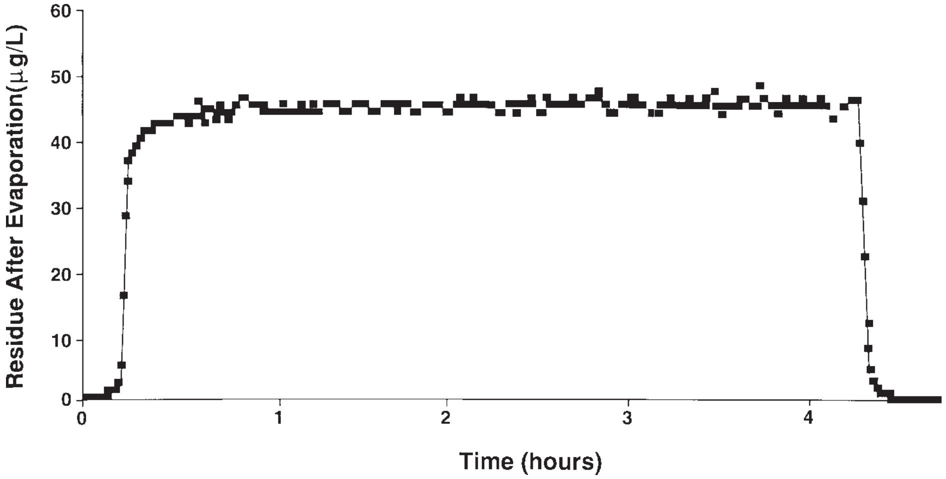

FIG. 5 Results for Test Method for Contaminant Injected at Constant Rate for 4 h

APPENDIX

(Nonmandatory Information)

X1. DISTINGUISHING BETWEEN CLEAN AND DIRTY WATER WITH A CONDENSATION NUCLEUS COUNTER (CNC)

X1.1 Like all other particle counters, the CNC 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 atomizer 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 CNC. Particles to the left of the efficiency curve do not initiate nucleation and are therefore not counted. Particles to the fight 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 atomizer 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 CNC's detection efficiency curve. As the high-purity water becomes dirtier, the number of residue particles able to initiate nucleation increases and the CNC counts more particles.

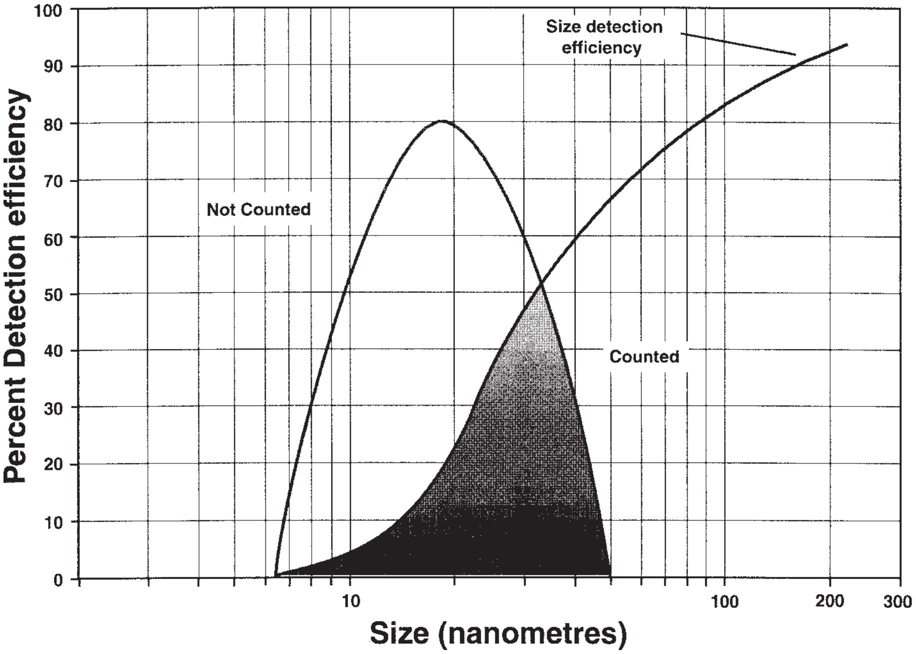

FIG. X1.1 Size Distribution of Residue from Clean Water

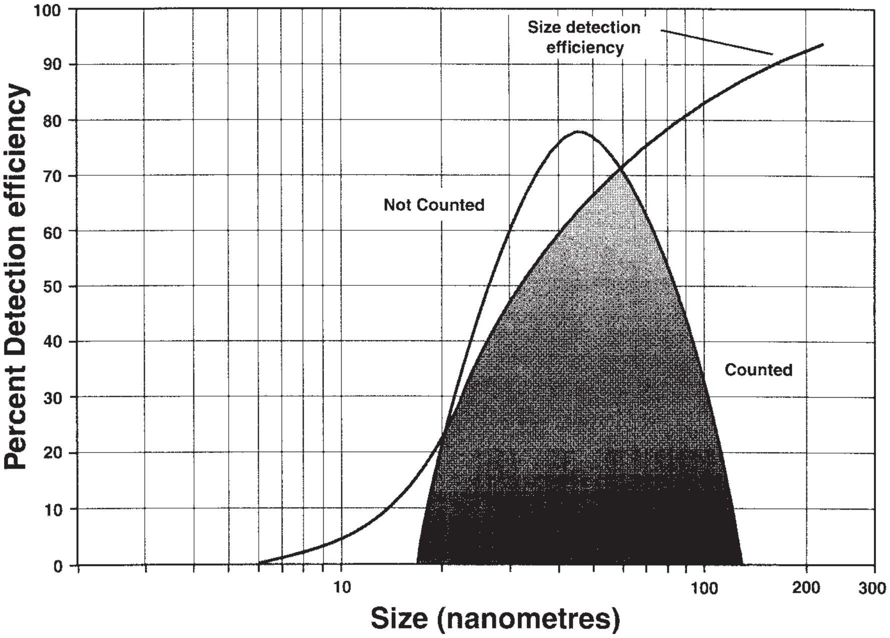

FIG. X1.2 Size Distribution of Residue from Dirty Water

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