Designation: D 4453 – 02

An American National Standard

Standard Practice for Handling of Ultra-Pure Water Samples[1]

This standard is issued under the fixed designation D 4453; 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 practice[2] covers concepts for handling ultra-pure water samples needed for the measurement of ever-decreasing levels of specified impurities that are encountered in the operation of modern high-pressure boilers and turbines. The handling of blanks associated with the analysis of ultra-pure water samples is also covered by this practice. The techniques presented can help the investigator increase the accuracy of analyses performed.

1.2 This practice is applicable to water and steam samples from "zero solids treated" once-through or drum-type boilers, reactor coolant water, electronic grade water, or any other process water where analyte concentrations are in the low parts per billion (micrograms per litre) range.

1.3 *This standard does not purport to address all of the safety problems, 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.* Specific hazards statements are given in 5.2.3.5, 5.1, and 5.3.7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[3]

D 1193 Specification for Reagent Water[3]

3. Significance and Use

3.1 The determination of trace impurities (on the order of parts per billion) in ultra-pure water places extreme requirements on all aspects of the analytical system. This is particularly true when ubiquitous species such as sodium and chloride are of interest because they can potentially be introduced as contaminants at almost every step of an analytical procedure. Contamination can occur during sample collection, during sample storage by leaching of improperly cleaned containers, during sample transfer, and by handling with pipets, syringes, etc., and during the actual analysis by contaminated reagents and sample cells and loop systems. It is also possible that trace contaminants can be lost from samples by volatilization or precipitation, by diffusion into the matrix of the container material, and by "plating out" on the walls of sampling lines by flow phenomena.

3.2 Strict adherence to a given procedure is necessary to achieve good results at trace levels of analysis because very small differences in procedure execution will affect precision and the addition or loss of nanogram amounts of analyte may affect the accuracy of a determination.

4. Reagents and Materials

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] 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.

4.2 *Purity of Water*— Reference to high-purity water shall be understood to mean water conforming to Specification D 1193, Type I reagent water, post treated with an organic removal cartridge or demineralized water which has additionally been polished using a cartridge water purification system with an organic removal cartridge and 0.2-µm final filter.

4.3 *Hydrochloric Acid* (1 + 1)—Dilute concentrated hydrochloric acid with an equal quantity of high purity water.

4.4 *Nitric Acid* (1 + 1)—Dilute concentrated nitric acid with an equal quantity of high purity water.

4.5 *Nitric Acid*, ultra-pure.

4.6 *Methanol*.

4.7 *n-hexane*.

4.8 *Nitrogen*, organic-free.

5. Procedure

5.1 *Environmental Conditions*—Any processes that might contaminate the analytes should be excluded from the sampling

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[1] This practice 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.

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[2] This practice suggests the use of specific techniques. As new techniques are developed or required by lower limits, revision of this practice will likely be needed.

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

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., 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 handling area, e.g., smoke, volatile organic solvents, etc. (**Warning**—when performing trace organic analyses, do not allow the use of volatile organic solvents or smoking at the same time and within the area.)

5.2 *Sample Containers and Their Treatment*:

5.2.1 *Analysis of Trace Metals*:[5]

5.2.1.1 Bottles made from the following materials should be adequate: TFE-fluorocarbon FEP, HDPE, LDPE, Polypropylene, and polycarbonate. Caps should be made of the same material or, if not available, the caps should be lined with one of the suggested materials.

5.2.1.2 Fill the bottle with HCl (1 + 1) and allow to stand for 48 h at room temperature (80°C for TFE-fluorocarbon), then empty and rinse with high purity water.

5.2.1.3 Fill the bottle with HNO_3 (1 + 1) and allow to stand for 48 h at room temperature (80°C for TFE-fluorocarbon), then empty and rinse with high purity water.

5.2.1.4 Fill the bottle about one third full with high purity water, cap, shake, and empty. Wear disposable polyethylene gloves when handling the bottles from this point onward. If a contaminated surface is touched, remove and replace the glove.

5.2.1.5 Repeat 5.2.1.4.

5.2.1.6 Completely fill the bottle with high purity water, cap, and allow to soak for 48 h. After filling, place the bottle in a polyethylene bag and seal the bag during the storage period. The high-purity water should be changed at weekly intervals during long storage periods.

5.2.2 *Analysis of Other Trace Ions*:[6]

5.2.2.1 Containers made from the following materials should be adequate: HDPE, LDPE, polysulfone, polycarbonate, polystyrene, polypropylene, and polymethyl pentene. The temperature of the samples should not be above 50°C when taken or during the storage period to prevent leaching from the containers. (See 5.3.3.)

5.2.2.2 Fill the bottle one third full with high purity water, cap, shake, and empty. Wear disposable polyethylene gloves when handling the bottles from this point onward. If a contaminated surface is touched, remove and replace the glove.

5.2.2.3 Repeat 5.2.2.2.

5.2.2.4 Completely fill the bottle with high purity water, cap, and allow to soak for a minimum of 1 day and a maximum of 5 days. After filling, place the bottle in a polyethylene bag and seal the bag during the storage period. The high-purity water should be changed at 5-day intervals during long storage periods.

5.2.3 *Analysis of Trace Organics (Acid and Base Neutrals)*:

5.2.3.1 The sample bottle must be borosilicate glass with a TFE-fluorocarbon-lined or aluminum-lined cap.

5.2.3.2 Wash in hot detergent water and rinse with tap water three times.

5.2.3.3 Rinse three times with high purity water.

5.2.3.4 Bottles must be either heated to a minimum of 400°C in a muffle furnace (or dry heat sterilizer) for at least 30 min or solvent rinsed as in 5.2.3.5.

5.2.3.5 Rinse with solvents in the following order: methanol, n-hexane. Gloves worn during the solvent rinse may contain plasticizers (phthalates) that may cause contamination. Polyurethane, polyethylene, or nitrile rubber gloves are not likely to have phthalates and should be used. (**Warning**—when rinsing with solvents, use a fume hood with proper exhaust flow.)

5.2.3.6 Dry with organic-free nitrogen to drive off the volatile solvents.

5.2.3.7 Immediately cap the bottle with a TFE-fluorocarbon-lined or aluminum-lined cap which has been previously cleaned using the same method.

5.2.4 *Analysis of Trace Volatile Organics*:

5.2.4.1 The sample container must be glass with a TFE-fluorocarbon-lined septum and screw cap properly tightened to provide a hermetic seal.

5.2.4.2 Wash in hot detergent water, and rinse with tap water three times.

5.2.4.3 Rinse three times with high-purity water.

5.2.4.4 Heat the vials and septa at 105°C for 1 h, then cool to room temperature in an enclosed contaminant-free area. Cap the vials with the TFE-fluorocarbon lining of the septum down.

5.3 *Sampling*:

5.3.1 Errors due to the sampling process can be minimized using an on-line measurement technique. A proper choice of materials to conduct the sample to the measuring instrument and the sample's residence time in transit can affect the final accuracy.

5.3.2 Some of the same precautions followed in the preparation of the sample containers must also be followed when collecting grab samples (see above). It is recommended that sample conditioning condensers, coolers, and associated fittings and valves be of stainless steel and maintained leak free (See Practice D 1066). Condensate temperature should be <50°C and preferably near ambient temperature.

5.3.3 Any samples to be stored more than 24 h should be refrigerated (4°C). Samples requiring trace $PO_4^{=}$, NO_3^{-}, NH_4^{+}, and $SO_4^{=}$ determinations should be refrigerated at 4°C at the time of collection. These species are subject to biological degradation.

5.3.4 Establish a continuous flow in a well-flushed sampling line (24 h recommended). Do not readjust the flow rate less than 45 min before sampling. (See Practice D 1066.)

5.3.5 Put on disposable polyethylene gloves before handling the sample bottle. Empty the bottle, rinse with the sample (including cap) three times, fill only to the rim to prevent ionic transport in the water film on the outside of the sample bottle. Replace the bottle in the plastic bag and collect a duplicate sample.

5.3.6 Samples collected for the analysis of non-alkali trace metals should be acidified to a pH of <2 with 1 mL of ultrapure HNO_3 per 500 mL of sample. The concentrated acid should be added to the sample bottle so as to keep its contact time with the bottle to a minimum.[7] Fill these bottles just to the rim to

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[5] Except alkali and alkali earth metals.

[6] Ions such as Na^+, K^+, Cl^-, Ca^{+2}, Mg^{+2}, F^-, Br^-, NH_4^+, NO_3^-, $SO_4^{=}$, and $PO_4^{=}$.

[7] This prevents the formation of ion-exchange sites on the bottle's internal surface.

avoid loss of the acid. Replace the bottle in the plastic bag and collect a duplicate sample.

5.3.7 When sampling for volatile organics the vial should be filled to overflowing so that a convex meniscus is formed. The cap and septum with the TFE-fluorocarbon side down is placed on the meniscus and sealed allowing no air into the vial. (**Warning**—avoid warming the bottle to prevent breakage.)

5.3.8 In the event an automatic sampler is being used, care must be taken during set-up, and blank water must be run through the sampler following the initial set-up to assure adequate rinsing prior to use.

5.4 *Analytical Blank*:

5.4.1 The ability to control the level of the analytical blank has seriously affected the accuracy of modern methods of trace element analysis. Often it is the variability in the blank correction and not the absolute value of the blank that affects the accuracy of the analysis. As the variability becomes a significant percentage of the sample amount, more determinations of the blank are necessary so that the variability can be estimated with some degree of reliability. It is a mistake to base the blank correction on a single determination. At least three replicate runs for the blank determination as well as the subsequent analyses of each sample are recommended.

5.4.2 All precautions observed in the preparation of bottles for sampling of ultra-pure water shall also be observed for bottles used in the preparation of analytical blanks.

5.4.3 When acidifying samples for trace metals, also acidify the blank with the same amount of acid.

6. Keywords

6.1 analysis; container; contamination; ion; sampling