



Standard Guide for Field Preservation of Groundwater Samples¹

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^{ε1} NOTE—Editorial changes were made throughout in May 2012.

1. Scope

1.1 This guide covers methods for field preservation of groundwater samples. Laboratory preservation methods are not described in this guide.

1.2 *This standard may involve hazardous materials, operations, and equipment. 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.*

1.3 *This guide offers an organized collection of information or a series of options and does not recommend a specific course of action. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this guide may be applicable in all circumstances. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "Standard" in the title of this document means only that the document has been approved through the ASTM consensus process.*

2. Referenced Documents

2.1 ASTM Standards:²

[D653 Terminology Relating to Soil, Rock, and Contained Fluids](#)

[D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents](#)

[D5903 Guide for Planning and Preparing for a Groundwater Sampling Event](#)

[D6089 Guide for Documenting a Ground-Water Sampling Event](#)

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² 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.

2.2 Other Documents:

Standard Methods for the Examination of Water and Wastewater, 20th ed., 1999³

*International Air Transport Association Dangerous Goods Regulations*⁴

U.S. EPA, Office of Solid Waste, SW-846, 3rd ed.

U.S. EPA, Title 40, Code of Federal Regulations, Part 136

U.S. DOT, Title 49, Code of Federal Regulations, Part 172

3. Terminology

3.1 *Definitions:* For definitions of common technical terms in this standard, refer to Terminology [D653](#).

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *chemical preservation*—the addition of acidic, alkaline or biologically toxic compounds, or combination thereof, to a groundwater sample to prevent changes in chemical properties of the sample that may occur after collection.

3.2.2 *holding time*—the maximum amount of time that may transpire from the moment a sample container is filled to the time the sample is extracted or analyzed. Holding times are parameter-specific, variable in length, and defined by laboratory analytical methods.

3.2.3 *physical preservation*—methods that are implemented to protect the physical integrity of a groundwater sample from the time the sample is collected until the sample is analyzed.

3.2.4 *temperature blank*—a quality control sample that is transported with samples and is used by the laboratory performing sample analyses to verify that temperature-sensitive samples have been adequately cooled to 4°C for shipment to and arrival at the laboratory (see [Note 1](#)).

NOTE 1—Forms of temperature blank include: (1) using a commercially prepared, fluid-filled bottle containing a permanently fixed National Institute of Standards and Technology (NIST)-certified (or NIST-traceable) thermometer, the temperature of which is read directly by the laboratory; (2) submission of a designated sample container filled with water (for example, groundwater, distilled water, or deionized water) that is opened by the laboratory and immediately measured for temperature of the water

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

⁴ Available from the Superintendent of Documents, US Government Printing Office, Washington, DC 20402.

using a National Institute of Standards and Technology-certified (or NIST-traceable) thermometer; or (3) submission of a designated container filled with water (for example, groundwater, distilled water, or deionized water) on which the laboratory uses a remote infrared temperature sensor to measure the temperature. Regardless of the method used, all measured temperatures are compared against the required temperature for each sample (for example, 4°C) in conjunction with a previously defined window of acceptable variance from this required temperature as documented in the sampling and analysis plan.

4. Significance and Use

4.1 Groundwater samples are subject to chemical, physical, and biological change relative to in-situ conditions at the ground surfaces as a result of exposure to ambient conditions during sample collection (for example, pressure, temperature, ultraviolet radiation, atmospheric oxygen, and contaminants) **(1) (2)**.⁵ Physical and chemical preservation of samples minimize further changes in sample chemistry that can occur from the moment the groundwater sample is retrieved, to the time it is removed from the sample container for extraction or analysis, or both. Measures also must be taken to preserve the physical integrity of the sample container.

4.2 The need for sample preservation for specific analytes should be defined prior to the sampling event and documented in the site-specific sampling and analysis plan in accordance with Guide **D5903**. The decision to preserve a sample should be made on a parameter-specific basis as defined by individual analytical methods.

5. Timing and Purpose of Groundwater Sample Preservation

5.1 Groundwater samples should be preserved in the field at the time of sample collection using physical means to prevent sample container breakage or temperature increases, and chemical means to minimize changes in groundwater sample chemistry prior to laboratory analysis.

6. Groundwater Sample Preservation Procedures

6.1 Groundwater sample preservation procedures are grouped into two general categories: (1) physical preservation and (2) chemical preservation. Preservation procedures should address the following details on a parameter-specific basis: sample container design and construction, protection from ultraviolet light, temperature control, chemical addition, and pH control measures **(2)**.

6.1.1 *Physical Preservation of Groundwater Samples*—Physical groundwater sample preservation methods include: (1) use of appropriate sample collection containers for each parameter being analyzed, (2) use of appropriate packing of sample containers for shipment to prevent sample container breakage and potential cross-contamination of samples during shipment, and (3) temperature control.

6.1.1.1 *Sample Container Selection*—Proper selection of containers for groundwater sample collection is an important means of protecting the integrity of the sample. Specifications on container design, including shape, volume, gas tightness,

materials of construction, and use of cap liners, are defined for specific parameters or suites of parameters (for example, amber glass containers protect photosensitive analytes such as (PCBs) from chemical alteration). Specifications for sample container selection are documented in parameter-specific analytical methods (for example, ASTM, U.S. EPA SW846, AWWA Standard Methods) as well as in Federal (40 CFR Part 136), state, and local regulatory guidelines on groundwater sample collection and preservation. The type of sample containers to be used in a sampling event should be determined during sampling event planning in accordance with Guide **D5903** and documented in the sampling and analysis plan as described in **8.1** of this guide and Guide **D6089**.

6.1.1.2 *Sample Container Packing and Shipping*—Field personnel should package and ship samples in compliance with all applicable regulations including the Department of Transportation (for example, Title 49 Code of Federal Regulations, Part 172) and the International Air Transportation Association (IATA). Sample containers should be shipped in a manner that will ensure the samples are received intact by the laboratory, at the appropriate temperature, and as soon as possible to allow sufficient time for the laboratory to perform the requested analyses within the holding time defined by the applicable laboratory analytical method for each parameter.

6.1.1.3 *Temperature Control*—Samples analyzed for some parameters (for example, nitrite) require temperature control. The temperature of these samples should be lowered to 4°C immediately after performing any field analyses required (for example, temperature or pH) and chemical preservation **(3)**. When necessary, temperature should be lowered as soon as possible and maintained at 4°C until the sample is analyzed. Sample temperatures can be lowered most efficiently using on-site refrigeration or wet ice. Wet ice may need to be replenished prior to shipping to maintain sample temperatures at 4°C. If required by regulation, dry ice may be used to cool samples, however, care should be taken to prevent sample freezing. Reuseable ice packs may be used to lower sample temperature, however, they often do not have the capacity to adequately lower or maintain temperatures, or both; consequently, their use is not recommended **(4)**. A temperature blank should be used with each shipping container of samples to determine actual sample temperatures at the time the sample shipment is received by the laboratory.

6.1.2 *Chemical Preservation of Groundwater Samples:*

6.1.2.1 Chemical preservation of groundwater samples involves the addition of one or more chemicals (reagent-grade or better) on a parameter-specific basis to protect sample integrity. **Appendix X1** provides examples of common analyte-specific chemical preservation methods.

6.1.2.2 Chemical preservation is specified in numerous analytical methods as well as in various regulatory guidance documents. Chemicals can be used to adjust sample pH or inhibit microbial activity to prevent chemical alteration of samples. Initial pH of samples should be determined prior to chemical preservation so appropriate chemical adjustment can be made.

6.1.2.3 Groundwater samples can be chemically preserved in one of several ways: (1) titration of pH-adjusting compounds

⁵ The boldface numbers in parentheses refer to the list of references at the end of this standard.

(for example, nitric acid) while monitoring pH change with a pH meter or narrow-range litmus paper; (2) addition of a premeasured volume of liquid preservative (for example, sulfuric acid) contained in glass vials or ampules to the sample container (Note 2); (3) addition of pelletized preservative (for example, sodium hydroxide) to the sample container; and (4) addition of preservative to empty sample containers prior to shipment of the empty containers to the field (that is, prepreserved sample containers) Note 3. After the sample container is filled and preserved, it should be securely capped and gently inverted to ensure uniform distribution of the preservative throughout the sample (see Note 4).

NOTE 2—Care should be taken not to add too large a volume of chemical preservative to prevent sample dilution. A generally accepted limit is 0.5 % maximum dilution.

NOTE 3—The use of prepreserved containers should be evaluated on a parameter-specific basis.

NOTE 4—Pelletized preservatives may take longer to dissolve and mix with the sample.

6.1.2.4 The end point of chemical preservation, designed to adjust pH to specific final pH levels, (for example, <2.0 or >12.0) should be verified in the field using narrow-range litmus paper (pH paper) or a properly calibrated pH meter. A small amount of sample can either be decanted into a separate container or a parallel sample can be collected for pH verification (for example, for samples containing light non-aqueous phases), rather than introducing foreign materials into the sample container being submitted for analysis. When collecting samples in prepreserved containers, care must be taken not to prerinse the container with the sample and to avoid overfilling the container to prevent loss of chemical preservative.

NOTE 5—Samples containing a light non-aqueous phase should not be chemically preserved with strong acid or base.

6.1.2.5 When using premeasured volume preservatives such as vials, ampules, or prepreserved containers, additional preservative should be provided by the laboratory and be available in the field to add to a sample if necessary to reach the required final pH. The additional preservative should be the same type, grade, and concentration as that used initially to preserve the sample (see Note 6, Note 7, and Note 8).

7. Timing of Groundwater Sample Preservation

7.1 Groundwater samples should be preserved immediately upon collection to minimize the time for chemical alteration of sample chemistry to occur (3). An exception is those samples requiring field filtration, which should be field-filtered first, then chemically preserved.

NOTE 6—When using ampules, care should be taken to avoid introducing glass shards or painted ampule surfaces into the sample container which could impact sample integrity (5).

NOTE 7—Even when following recommended chemical preservation methods, chemical reactions may occur (2). For example, water containing high concentrations of calcium carbonate may effervesce when

acidified. In these cases, modifications of sample preservation methods may be necessary, such as collecting an unpreserved sample or using alternate chemical preservatives. Any modifications must be pre-approved by regulatory agencies and laboratories involved, and allowed by the sampling and analysis plan.

NOTE 8—It may be necessary to establish site-specific protocol to address acceptable periods for storage and storage conditions for prepreserved sample containers due to the potential for chemical reactions to occur between the chemical preservative and the empty sample container.

8. Report

8.1 Records should be kept for all forms of sample preservation used for groundwater samples. Report the following in accordance with Guide D6089:

8.1.1 Type of sample container(s) used for each parameter being analyzed (volume, materials of construction, type of cap, and so forth);

8.1.2 Number of each type of sample container actually filled;

8.1.3 Packaging method(s) used to prevent sample bottle breakage during sample storage and shipment;

8.1.4 Temperature and pH of groundwater samples at the time of sample collection;

8.1.5 How groundwater samples were cooled to 4°C, if required for physical preservation;

8.1.6 Sample temperature at the time of sample shipment;

8.1.7 Chemical preservative(s) used on a parameter-specific basis:

8.1.7.1 What chemicals were added, by whom, time, and date,

8.1.7.2 Specifications (if known) on actual preservative(s) used (that is, source, manufacturer, grade, lot number, and so forth),

8.1.7.3 How the chemical preservative was added,

8.1.7.4 Volume of chemical preservative added (if known), and

8.1.7.5 Results of field preservation verification tests when pH is adjusted (initial and after preservation).

8.1.8 Elapsed time between sample collection and preservation;

8.1.9 Description of appearance of unpreserved and preserved samples, specifically noting any chemical reactions which may occur upon addition of chemical preservative (for example, effervescence, formation of precipitates, change in color);

8.1.10 Description of the source of sample containers used;

8.1.11 Description of temperature blank(s) submitted along with the samples: how prepared, how many submitted, and how blank was identified;

8.1.12 Completed Chain of Custody forms (if used); and

8.1.13 Name(s) of the individuals taking the samples.

9. Keywords

9.1 chemical preservation; groundwater sampling; holding time; physical preservation; preservative; sample preservation; temperature blank

APPENDIX
(Nonmandatory Information)
X1. EXAMPLES OF CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS MATRICES

 See **Table X1.1**.

TABLE X1.1 Examples of Containers, Preservation Techniques, and Holding Times for Aqueous Matrices^A

Name	Container ^B	Preservation	Minimum Holding Time
Inorganic Tests:			
Chloride	P, G	None required	28 days
Cyanide, total and amenable to chlorination	P, G	Cool to 4°C; if oxidizing agents present add 5 mL 0.1 N Na ₂ A ₂ O ₂ per L or 0.06 g of ascorbic acid per L; adjust pH >12 with 50 % NaOH. See Method 9010 for other interferences.	14 days
Nitrate	P, G	Cool to 4°C	48 hours
Sulfate	P, G	Cool to 4°C	28 days
Sulfide	P, G	Cool to 4°C, add zinc acetate	7 days
Metals:			
Chromium VI	P, G	Cool to 4°C	24 hours
Mercury	P, G	HNO ₃ to pH <2	28 days
Metals, except chromium VI and mercury	P, G	HNO ₃ to pH <2	6 months
Organic Tests:			
Acrolein and acrylonitrile	G, PTFE-lined septum	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C , Adjust pH to 4-5	14 days
Benzidines	G, PTFE-lined cap	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C	7 days until extraction, 40 days after extraction
Chlorinated hydrocarbons	G, PTFE-lined cap	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C	7 days until extraction, 40 days after extraction
Dioxins and furans	G, PTFE-lined cap	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C	30 days until extraction, 45 days after extraction
Haloethers	G, PTFE-lined cap	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C	7 days until extraction, 40 days after extraction
Nitroaromatics and cyclic ketones	G, PTFE-lined cap	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C , store in dark	7 days until extraction, 40 days after extraction
Nitrosamines	G, PTFE-lined cap	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C , store in dark	7 days until extraction, 40 days after extraction
Oil and grease	G	Cool to 4°C, add 5 mL diluted HCl	28 days
Organic carbon, total (TOC)	P, G	Cool to 4°C, store in dark ^D	28 days
Organochlorine pesticides	G, PTFE-lined cap	Cool to 4°C	7 days until extraction, 40 days after extraction
Organophosphorus pesticides	G, PTFE-lined cap	Cool to 4°C ^E	7 days until extraction, 40 days after extraction
PCBs	G, PTFE-lined cap	Cool to 4°C	7 days until extraction, 40 days after extraction
Phenols	G, PTFE-lined cap	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C	7 days until extraction, 40 days after extraction
Phthalate esters	G, PTFE-lined cap	Cool to 4°C	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons	G, PTFE-lined cap	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C , store in dark	7 days until extraction, 40 days after extraction
Purgeable aromatic hydrocarbons	G, PTFE-lined septum	Cool to 4° C, 0.008 % Na ₂ S ₂ O ₃ ^{C,D}	14 days
Purgeable halocarbons	G, PTFE-lined septum	Cool to 4°C, 0.008 % Na ₂ S ₂ O ₃ ^C	14 days
Total organic halides (TOX)	G, PTFE-lined cap	Cool to 4°C, adjust to pH<2 with H ₂ SO ₄	28 days
Radiological Tests:			
Alpha, beta, and radium	P, G	HNO ₃ to pH<2	6 months

^A Table originally excerpted, in part, from Table II, 49 FR 28, Oct. 26, 1984, and revised as appropriate for SW-846. See Chapter Three, Chapter Four, or Section 6.0 of the individual methods for more information.

^B Polyethylene (P) or Glass (G)

^C Free chlorine must be removed by the appropriate addition of Na₂S₂O₃.

^D Adjust to pH<2 with H₂SO₄, HCl, or solid NaHSO₄. Free chlorine must be removed prior to adjustment.

^E Adjust samples to pH 5-8 using NaOH or H₂SO₄.

^F Other sources of preservation methods are available (for example, Practice D3694, Standard Methods, USGS OFR 95-352) and may include methods for additional parameters.

REFERENCES

- (1) Parr, J., Bollinger, M., Callaway, O., and Carlberg, K., *Preservation Techniques for Organic and Inorganic Compounds in Water Samples*, Chapter 14, *Principles of Environmental Sampling*, American Chemical Society Professional Reference Book, 1988, pp. 221–230.
- (2) Keith, L.H., “Environmental Sampling: A Summary,” *Environmental Science and Technology*, Vol 24, No. 5, 1990, pp. 610–617.
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- (4) Kent, R.T., and Payne, K.E., *Sampling Groundwater Monitoring Wells: Special Quality Assurance and Quality Control Considerations*, Chapter 15, *Principles of Environmental Sampling*, American Chemical Society Professional Reference Book, 1988, pp. 231–246.
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