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Standard Guide for Spiking into Aqueous Samples ¹

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1. Scope

1.1 This guide covers the general technique of “spiking” a broad range of materials into aqueous media. This guide will serve the analyst in preparing spiked samples for quality control purposes. Guidance is also provided to aid the analyst in calculating recoveries and interpreting results. It is the responsibility of the analyst to determine whether the procedures and materials described here are appropriate to the task at hand.

1.2 The procedures in this guide are focused on “matrix spike” preparation, analysis, and interpretation of results. The applicability of these procedures to the preparation of calibration standards, calibration check standards, laboratory control standards, reference materials, and other quality control materials by spiking is incidental. A sample (the matrix) is fortified (spiked) with the analyte of interest for a variety of analytical and quality control purposes. While the spiking of multiple sample portions is discussed, the method of standard additions is not covered.

1.3 This guide is intended for use in conjunction with the individual analytical test method that provides procedures for analysis of the analyte or component of interest. The test method is used to determine an analyte or component’s background level and, again after spiking, its now elevated level. Each test method typically provides procedures not only for samples, but also for calibration standards or analytical control solutions, or both. These procedures include preparation, handling, storage, preservation, and analysis techniques. These procedures are applicable by extension, using the analyst’s judgement on a case-by-case basis, to spiking solutions, and are not reiterated in this guide. See also Practice **E200** for preparation and storage information.

1.4 These procedures apply only to analytes that are soluble in water at the concentration of the spike plus any background material, or to analytes soluble in a solvent that is itself water-soluble. The system used in the later case must result in

a homogeneous solution of analyte and sample. Meaningful recovery data cannot be obtained if an aqueous solution or homogenous suspension of the analyte of interest in the sample cannot be attained. These procedures may be applicable to microbiological preparations if the homogeneity of the suspension can be adequately maintained throughout the course of the analysis, for example, by mechanical agitation or stirring.

1.5 Matrix spiking may be performed in the field or in the laboratory, depending on which part of the analytical process is to be tested. Field spiking tests the recovery of the overall process, including preservation and shipping of the sample. Laboratory spiking tests the laboratory process only. Spiking of sample extracts, concentrates, or dilutions will test only that portion of the process subsequent to addition of the spike.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

- D1129** Terminology Relating to Water
- D1193** Specification for Reagent Water
- D3694** Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
- D3856** Guide for Management Systems in Laboratories Engaged in Analysis of Water
- D4375** Practice for Basic Statistics in Committee D19 on

¹ This guide is under the jurisdiction of ASTM Committee **D19** on Water and is the direct responsibility of Subcommittee **D19.02** on Quality Systems, Specification, and Statistics.

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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.

Water (Withdrawn 2018)³
**E200 Practice for Preparation, Standardization, and Storage
 of Standard and Reagent Solutions for Chemical Analysis**

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this standard, refer to Terminology **D1129**.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *matrix spike, n*—the quantity (mass) of a component (analyte) of interest that is added to a sample (matrix) in order to test the bias as measured by recovery (of that component under specific analytical conditions) and reported as percent recovery (*P*).

3.2.2 *spike, v*—the addition of a known amount of an analyte of known identity to a measured volume of a sample (from a specific matrix) to determine the efficiency with which the added analyte can be “recovered” from (measured in) that matrix by the analytical system after exposure to a specific portion of an analytical process. Matrix spiking is a process for accomplishing this. The precision and bias estimates from several trials under specific analytical conditions represent the measurement efficiency with which the analyte may be determined under these conditions.

3.2.3 *spiking solution, n*—the solution in which one or more spikes are dissolved (along with any necessary preservatives). This solution acts as a carrier to provide ease of measurement and more rapid and thorough mixing of the spike into the sample, as compared to adding the spike as a pure compound.

4. Summary of Guide

4.1 This guide describes a technique for the addition of a known amount of an analyte to an aqueous sample. Appropriate concentrations of the spike relative to the original concentration in the sample are discussed. Applications of the technique and aids in the interpretation of results obtained are described.

5. Significance and Use

5.1 Matrix spiking is commonly used to determine the bias under specific analytical conditions, or the applicability of a test method to a particular sample matrix in that context, by determining the extent to which the spiked analyte or component is recovered from the sample matrix under these conditions. Reactions or interactions of the analyte or component of interest with the sample matrix may cause a significant positive or negative effect on recovery and may render the chosen analytical, or monitoring, process ineffectual for that sample matrix.

5.2 Matrix spiking can also be used to monitor the performance of a laboratory, individual instrument, or analyst as part of a regular quality assurance program. Changes in spike recoveries or recovery limits from the same or similar matrices over time may indicate variations in the quality of analytical results.

5.3 Spiking can be used to compare the recoveries of like spikes from reagent water samples and natural matrix samples (measured with and without spike) to distinguish between (1) unusual interference and (2) inherent method recovery and instability effects. This guide does not attempt to deal with the statistical significance of differences in spike recoveries from different matrices.

5.4 Special precautions shall be observed when nonlaboratory personnel perform spiking in the field. It is recommended that all spike preparation work be performed in a laboratory by experienced analysts so that the field operation consists solely of adding a prepared spiking solution to the sample matrix. Training of field personnel and validation of their spiking techniques are necessary to ensure that spikes are added accurately and reproducibly. Duplicate field spikes can be used to document the reproducibility of the technique. When environmentally labile compounds are used as spikes, the spiking solution shall be protected up to the point of use by appropriate means such as chilling, protection from sunlight and oxygen, or chemical preservation.

NOTE 1—Any field spiked sample, if known to the laboratory, should be labeled as a field spike in the final results report. Also, whenever possible, field spiking of volatile compounds should be avoided.

5.5 It is often tacitly assumed that an analyte component is recovered from samples to approximately the same extent that a spike of the same analyte is recovered from a spiked sample. One reason that this assumption may be incorrect is that the spike may not be bound up in the sample (for example, with suspended matter) in the same way that the naturally occurring analyte is bound in the sample. The spike may therefore be recovered from the sample differently than the background level of the analyte. It is not good practice to correct analytical data using spike recoveries for this reason, as well as the fact that bias corrections can add variability. However, spike recovery information should be reported along with related sample analysis results.

5.6 This guide is also applicable to the use of spikes for quantification by the method of standard additions and to the addition of surrogates and internal standards.

6. Apparatus

6.1 *Pipetters*—Plunger-actuated pipetters, to dispense small volumes of spike solutions. These must be calibrated and tested carefully for repeatability before use.

6.2 *Volumetric Transfer Pipets*—Class A, used to deliver known volumes of sample and to add larger volumes of spiking solutions.

6.3 *Volumetric Flasks*—Class A volumetric flasks may be used to measure known volumes of sample.

6.4 *Balance*—An analytical (0.1-mg), semimicro (0.01-mg), or micro (0.001-mg) balance.

7. Reagents

7.1 *Purity of Reagents*—At a minimum, reagent grade chemicals shall be used in all spike preparations. Reagents of the highest available purity shall be used for spike analytes and

³ The last approved version of this historical standard is referenced on www.astm.org.