Designation: E2677 – 14

Standard Test Method for Determining Limits of Detection in Explosive Trace Detectors[1]

This standard is issued under the fixed designation E2677; 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 In harmony with the Joint Committee for Guides in Metrology (JCGM) and detection concepts of the International Union of Pure and Applied Chemistry (IUPAC) (**1**, **2**, **3**)[2], this test method uses a series of replicated measurements of an analyte at dosage levels giving instrumental responses that bracket the critical value, a truncated normal distribution model, and confidence bounds to establish a standard for determining practical and statistically robust limits of detection to analytes sampled on swabs by explosive trace detectors (ETDs).

1.2 Here, the limit of detection (LOD90) is defined to be the lowest mass of a particular compound deposited on a sampling swab for which there is 90 % confidence that a single measurement in a particular ETD will have a true detection probability of at least 90 % and a true nondetection probability of at least 90 % when measuring a process blank sample.

1.3 This particular test method was chosen on the basis of reliability, practicability, and comprehensiveness across tested ETDs, analytes, and deployment conditions. The calculations involved in this test method are published elsewhere (**4**), and may be performed consistently with an interactive web-based tool available on the National Institute of Standards and Technology (NIST) site: http://pubapps.nist.gov/loda.

1.4 *Intended Users*—ETD developers, ETD vendors, ETD buyers, ETD testers, ETD users (first responders, security screeners, and the military), and agencies responsible for public safety and enabling effective deterrents to terrorism.

1.5 While this test method may be applied to any detection technology that produces numerical output, the procedures have been designed for ion mobility spectrometry (IMS) based ETD systems and tested with low vapor pressure explosive compounds. Compounds are deposited as liquid solutions on swabs and dried before use. As some swabs are absorbent, this deposition procedure may not be optimal for those ETD technologies that rely on high coverage of analyte on the surface of the swab. Background interferences introduced to the test samples were representative of a variety of conditions expected during deployment, but these conditions were not intended as comprehensive in representing all possible scenarios. The user should be aware of the possibility that untested scenarios may lead to failure in the determination of a reliable LOD90 value.

1.6 *Units*—The values stated in SI units are to be regarded as the 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 and health practices and determine the applicability of regulatory limitations prior to use. Some specific hazards statements are given in Section 8 on Hazards.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D6091 Practice for 99 %/95 % Interlaboratory Detection Estimate (IDE) for Analytical Methods with Negligible Calibration Error

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E288 Specification for Laboratory Glass Volumetric Flasks

E456 Terminology Relating to Quality and Statistics

E542 Practice for Calibration of Laboratory Volumetric Apparatus

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E969 Specification for Glass Volumetric (Transfer) Pipets

E1154 Specification for Piston or Plunger Operated Volumetric Apparatus

[1] This test method is under the jurisdiction of ASTM Committee E54 on Homeland Security Applications and is the direct responsibility of Subcommittee E54.01 on CBRNE Sensors and Detectors.

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[2] The boldface numbers in parentheses refer to a list of references at the end of this standard.

[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.

E1323 Guide for Evaluating Laboratory Measurement Practices and the Statistical Analysis of the Resulting Data
E2520 Practice for Verifying Minimum Acceptable Performance of Trace Explosive Detectors
E2655 Guide for Reporting Uncertainty of Test Results and Use of the Term Measurement Uncertainty in ASTM Test Methods

3. Terminology

3.1 *Definitions:*

3.1.1 *alarm rule, n*—user-selectable explosive trace detector (ETD) response requirements that, if met during an analysis, result in a detection alarm for a particular compound.

3.1.1.1 *Discussion*—An alarm rule is a logistical pattern in the detection response matrix for an analysis. The simplest alarm rule would require only a single positive detection response, whereas a more selective rule (useful for minimizing alpha risk) may require two positive responses in any of three channels and perhaps a negative response in another channel.

3.1.2 *alarm threshold, n—see* detection threshold.

3.1.3 *alpha, α, risk, n*—probability of obtaining a positive detection outcome, or alarm, when analyzing a process blank in a properly-operating ETD.

3.1.4 *analyte, n*—the particular chemical compound under consideration.

3.1.4.1 *Discussion*—Pure analyte is used to make reference solutions by quantitative dissolution into a known amount of solvent. Quantitative depositions of reference solutions are subsequently used to prepare reference swabs containing known amounts of analyte.

3.1.5 *beta, β, risk, n*—probability of obtaining a negative detection outcome, or non-alarm, in a properly operating ETD when analyzing a swab containing analyte at the mass level corresponding to the limit of detection.

3.1.6 *blank, n*—sample swab devoid of analyte.

3.1.6.1 *Discussion*—If a swab is prepared using the same procedures used in preconditioning the reference swabs and only pure solvent or a chemical background is deposited, this swab is called a process blank.

3.1.7 *chemical background, n*—particular mixture of environmental and ambient substances that may be sampled by a swab during normal operation of an ETD in a deployment area.

3.1.7.1 *Discussion*—The presence of certain substances on a sample or reference swab may interfere with or suppress expected ETD responses for particular analytes, hence influencing the effective limit of detection (LOD90) values for those analytes and changing the alpha and beta risks for the detection process.

3.1.8 *critical value, CV, n*—instrumental response amplitude at which there is particular confidence that the signal may be attributed to a particular analyte.

3.1.8.1 *Discussion*—The CV is defined by the desired alpha and beta risks of detection and is a response somewhat below the mean response of samples prepared at the limit of detection. A realistic CV is the optimal basis of a single-channel detection threshold.

3.1.9 *detection outcome, n*—binomial (yes/no) response of an analysis within a particular channel (or spectral window) in an ETD.

3.1.9.1 *Discussion*—The channel response is "positive" when the signal in the channel meets or exceeds all detection thresholds; otherwise, the channel response is "negative."

3.1.10 *detection threshold, n*—set of signal characteristics, often user selected, for a particular channel (or spectral window) in an ETD.

3.1.10.1 *Discussion*—These characteristics usually include the peak amplitude (optimally, the critical value) but may also include the peak shape, onset time, duration, and position within a detection window. If the measured signal in that channel meets or exceeds the detection threshold settings, the detection outcome is designated as "positive;" otherwise, the response is "negative." One or more position detections are needed within the alarm rules to elicit an alarm for a particular analyte. The alarm threshold for a particular analyte is the same as the detection threshold if the alarm rule uses only one channel. If the alarm rule requires two or more positive responses, or negative responses in certain channels, the alarm threshold is a logistical function of the channel signals involved.

3.1.11 *explosive trace detector, ETD, n*—device used to identify the presence of small amounts of explosive compounds.

3.1.11.1 *Discussion*—ETDs are commonly used at airports by security screeners, who wipe a surface with a swab to collect residues, and then analyze the swab in the ETD. Explosive vapor detectors (EVDs) are a subset of ETDs that sample air to detect vapors indicative of explosives.

3.1.12 *explosive vapor detector, EVD, n*—used to sample air—indoors, outdoors, or within containers—to identify vapors indicative of the presence of explosives.

3.1.12.1 *Discussion*—Detected vapors may be explosive compounds or other chemicals in patterns suggestive of particular explosive formulations.

3.1.13 *ion mobility spectrometry, IMS, n*—detection technology commonly used in commercial ETDs (for other technologies, please see Caygill et al (**5**).

3.1.13.1 *Discussion*—Typically, samples are heated to vaporize trace analytes of interest, which are then selectively ionized, separated on the basis of ion mobility through air in an analyzer tube, and detected using a Faraday cup. Raw responses are processed to enhance the chemical signals. Further information on IMS may be found in Eiceman and Zarpas (**6**).

3.1.14 *limit of detection, LOD, n*—commonly accepted as the smallest amount of a particular substance that can be reliably detected in a given type of medium by a specific measurement process.

3.1.14.1 *Discussion*—May be defined either in terms of the instrumental signal response or the analyte mass that elicits the signal response. Here, the limit of detection (LOD90) is defined to be the lowest mass of an analyte deposited on a reference swab for which there is 90 % confidence that a single measurement in particular ETD will have a true detection probability of at least 90 % and a true nondetection probability

of at least 90 % when measuring a process blank sample. Values of LOD90 are performance measures of a deployed detection system and provide guidance for setting optimal ETD detection thresholds in that system.

3.1.15 *LOD90, n—see* limit of detection.

3.1.16 *nondetection probability, n—see* beta risk.

3.1.17 *process blank, n—see* blank.

3.1.18 *reference swabs, n—see* swabs.

3.1.19 *significant mass level, SML, n*—lowest mass in a series of prepared mass levels that elicits significantly higher mean responses in an ETD compared to the mean responses from process blanks.

3.1.19.1 *Discussion*—The SML is a crude estimate of the LOD90.

3.1.20 *substrates, n—see* swabs.

3.1.21 *swabs, n*—also known as substrates, swipe media, traps, and wipes, swabs are special fabrics made of such materials as cotton, fiberglass, or polymers and are designed for wiping sample surfaces and holding residues collected from those surfaces.

3.1.21.1 *Discussion*—Distributed by ETD manufacturers and consumable suppliers, swabs have particular properties and shapes designed to fit into the sampling inlets of ETDs. Each type of swab has a "sweet spot" for sampling where the detection of analyte is optimized (Practice E2520). This is generally an area about 1 cm in diameter. Please consult with the manufacturer to confirm the location of the sweet spot. Swabs containing known amounts of analyte deposited in the sweet spot are called reference swabs.

3.1.22 *swipe media, n—see* swabs.

3.1.23 *traps, n—see* swabs.

3.1.24 *wipes, n—see* swabs.

4. Summary of Test Method

4.1 Reference solutions are prepared containing known concentrations of a particular analyte.

4.2 Standard operating conditions for the ETD are set. If needed, the target analyte is programmed into the ETD database.

4.3 *Optional*—Using a reproducible method, clean swabs are preconditioned with "chemical background."

4.4 The ETD is determined to be in operational readiness.

4.5 Exploratory measurements are performed to determine the significant mass level (SML), which is the lowest level of analyte mass on a reference swab that gives a mean response significantly higher than that from process blanks.

4.6 Using the SML as a guide, four mass levels of reference swabs are prepared that provide appropriate bracketing of the estimated LOD90 value.

4.7 Starting at the lowest mass level, replicates of the reference swabs are run on the ETD. In turn, the higher mass levels are run.

4.8 Data are evaluated using a validated algorithm accessed through a web-based calculator at http://pubapps.nist.gov/loda. This process returns an estimate of the LOD90 value as well as upper confidence and tolerance limits. Optional tools include data plotting and outlier tests. The alpha and beta risks may be changed from the default values.

4.9 Guidance is given regarding the setting of an alarm threshold in an ETD to achieve a reliable balance of alpha and beta risks.

5. Significance and Use

5.1 ETDs are used by first responders, security screeners, the military, and law enforcement to detect and identify explosive threats quickly. ETDs typically operate by detecting chemical agents in residues and particles sampled from surfaces and can have detection limits for some compounds extending below 1 ng. An ETD is set to alarm when its response to any target analyte exceeds a programmed threshold level for that analyte. Factory settings of such levels typically balance sensitivity and selectivity assuming standard operating and deployment conditions.

5.2 A LOD is commonly accepted as the smallest amount of a particular substance that can be reliably detected in a given type of medium by a specific measurement process (**2, 3**). The analytical signal from this amount shall be high enough above ambient background variation to give statistical confidence that the signal is real. Methods for determining nominal LOD values are well known (for example, Hubaux and Vos (**7**) and Practice D6091), but pitfalls exist in specific applications. Vendors of ETDs often report detection limits for only a single compound without defining the meaning of terms or reference to the method of determination.

NOTE 1—There are several different "detection limits" that can be determined for analytical procedures. These include the minimum detectable value, the instrument detection limit, the method detection limit, the limit of recognition, and the limit of quantitation. Even when the same terminology is used, there can be differences in the LOD according to nuances in the definition used, the assumed response model, and the type of noise contributing to the measurement.

5.3 When deployed, individual ETD performance (for example, realistic LODs) is influenced by: (*1*) ETD manufacturing differences, history, and maintenance; (*2*) ETD operating configurations (for example, thermal desorption temperature, analyzer temperature, and type of swab); and (*3*) environmental conditions (for example, ambient humidity and temperature and chemical background). As a result, realistic LOD values for an ETD may be poorly estimated by the factory specifications. These fundamental measures of ETD performance are critically important for assessing the ability of an ETD to detect trace levels of particular compounds in a particular setting, so a reliable and accessible method is needed to determine realistic LOD values, especially in the field.

5.4 *Technical Challenges and Pitfalls to the Determination of LOD Values in ETDs and the Setting of Optimal Alarm Thresholds:*

5.4.1 *Scope*—There are over 230 explosive materials currently listed by the Bureau of Alcohol, Tobacco, Firearms, and

Explosives.[4] There are many technologies used for detection, and ETD manufacturers design their systems and balance operating conditions to provide detection capabilities across as many analytes as possible. However, a very limited subset of analytes is normally used to test and verify ETD performance. Therefore, default ETD operating conditions and alarm thresholds may not be optimally set to detect reliably certain compounds deemed important in particular scenarios.

5.4.2 *Environment*—Ambient conditions and chemical background vary with the deployment location, which would influence ETD response sensitivities and LOD values.

5.4.3 *Risk Tolerance and Balance*—Values of alpha risk (false positive probability of process blanks) and beta risk (false nondetection probability of analytes at the detection limit) should be balanced and set according to security priorities (for example, alert level, probable threat compounds, throughput requirements, human factors, and risk tolerance). The default risk balance in an ETD may not be adequate for the deployment situation.

5.4.4 *Signal Variability (Heteroscedasticity)*—The variance in instrument response may not be consistent across analyte mass levels introduced into the ETD. In ion mobility spectrometry (IMS)-based technologies, the physicochemical mechanisms underlying atmospheric pressure ionization (with a finite number of available reactant ions) and ion mobility separation may be non-uniform across the ETD response regions. Typical methods of LOD determination usually assume constant variance.

5.4.5 *Proprietary Signal Processing*—Typical LOD determinations assume Gaussian distributions and use background variation as an important parameter. Unfortunately, alarm decisions in ETDs are rarely based on raw measurement signals; rather, proprietary algorithms are used to process the raw measurements. This processing may attempt to minimize alpha risk by truncating or dampening background signals, so background signals may be absent or the true distribution in these processed signals may be non-Gaussian, confounding the calculation of an accurate LOD.

5.4.6 *Multivariate Considerations*—To improve selectivity and decrease alpha risk, alarm decisions in ETDs may be based on multiple-peak responses rather than a single-peak amplitude measurement. Additionally, efforts to recognize and quantify unique ion fragmentation patterns across both the thermal desorption and drift-time domains are being developed for next-generation detectors.

5.4.7 *Diversity of Technologies*—The wide variety of ETDs on the market and those under development challenge general response models for accurate estimation of LOD.

5.4.8 *Security*—LOD values for explosives in ETDs cannot be openly published because of security and classification issues.

6. Apparatus

6.1 Dispensing device calibrated to deliver 1.00-µL aliquots.

6.2 ETD in operational readiness.

[4] Available from http://www.gpo.gov/fdsys/pkg/FR-2012-09-20/pdf/2012-23241.pdf.

7. Reagents and Materials

7.1 Reference solutions as prepared in 9.2.

7.1.1 Analyte.

7.1.2 Suitable solvent.

7.1.3 Volumetric flasks (10 mL).

7.1.4 Pipette to deliver 1-mL aliquots.

7.1.5 Amber 1- and 10-mL vials with tight caps.

7.2 Clean swabs designed for the particular ETD.

7.2.1 *Optional*—Chemical background or interferent/suppressant for treatment of clean swabs.

8. Hazards

8.1 Safety Data Sheets (SDS) for all chemicals, such as analytes and solvents, should be consulted before use. The user of this test method should also be aware of the hazards associated with the operation of the chosen ETD. While not ordinarily considered a hazard, the user should also be aware that many ETDs contain radioactive materials, which are either "Generally Licensed" by the Nuclear Regulatory Commission or "Exempt from Licensing." In either case, this may require radiation management and safety training in some organizations.

9. Procedure

9.1 Reference swabs shall be prepared containing the analyte at known levels within the sweet spot with an uncertainty of less than 5 %. A few organizations use drop-on-demand inkjet printing for the purpose (**8, 9**), but since these dispensing systems are not widely available, we recommend the traditional approach in which standard solutions are prepared and dispensed using a calibrated dispensing device that can deliver 1.00-µL aliquots. This small volume will help prevent excessive wicking of the analyte outside the sweet spot or into the interior of the swab. Please consult with the swab manufacturer to confirm the location of the sweet spot. Calibrations of volumetric flasks and pipettes and resulting LOD90 bias from these sources are not specifically covered in this test method, but procedures are available elsewhere (Practices E200 and E542 and Specifications E288 and E969).

9.2 *Preparation of Reference Solutions*—Reference solutions are prepared containing known concentrations of a particular analyte.

9.2.1 Analyte solutions at the following concentrations in a suitable solvent. An analytical-grade C2-C5 alcohol or acetonitrile is suitable for most explosive analytes; however, the blank solvent should be tested for undesired responses in the ETD before proceeding. The solute range (covering four orders of magnitude) should cover the performance capabilities of most ETDs for most analytes. If the approximate LOD value is known, this list may be shortened accordingly. For example, if LOD90 ≈ 1 ng for a particular analyte, then only Solutions A, E, and F need to be prepared, as discussed in 9.7.1.

9.2.1.1 *Solution A*—0.00 ng/µL (fluid used for process blank preparation).

9.2.1.2 *Solution B*—0.01 ng/µL.

9.2.1.3 *Solution C*—0.03 ng/µL.

9.2.1.4 *Solution D*—0.10 ng/µL.

9.2.1.5 *Solution E*—0.30 ng/µL.