Designation: E2677 – 20

Standard Test Method for Estimating Limits of Detection in Trace Detectors for Explosives and Drugs of Interest[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**)[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 estimating practical and statistically robust limits of detection.

NOTE 1—Other standards are available that evaluate the general performance of detection technologies for various analytes in complex matrices (for example, Practice E2520).

1.2 Here, the limit of detection (LOD90) for a compound is defined to be the lowest mass of that compound deposited on a sampling swab for which there is 90 % confidence that a single measurement in a particular trace detector 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 trace detectors, analytes, and deployment conditions. The calculations involved in this test method are published elsewhere (**3**), and are performed through an interactive web-based calculator available on the National Institute of Standards and Technology (NIST) site: https://www-s.nist.gov/loda.

1.4 *Intended Users*—Trace detector developers and manufacturers, vendors, testing laboratories, 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 method is especially applicable to measurement systems influenced by heterogeneous error sources that lead to non-linear and heteroskedastic dose/response relationships and truncated or censored response distributions at low analyte levels. The procedures have been tested using explosive and drug compounds in trace detectors based on ion mobility spectrometry, gas chromatography, and mass spectrometry (**4**). Compounds are deposited as liquid solutions on swabs and dried before use. 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 estimation 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Some specific hazards statements are given in Section 8 on Hazards.*

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:*[3]

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

[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.

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
E1323 Guide for Evaluating Laboratory Measurement Practices and the Statistical Analysis of the Resulting Data
E2520 Practice for Measuring and Scoring Performance of Trace Explosive Chemical Detectors
E2655 Guide for Reporting Uncertainty of Test Results and Use of the Term Measurement Uncertainty in ASTM Test Methods
E2771 Terminology for Homeland Security Applications

3. Terminology

3.1 *Definitions (also see Terminology E2771):*

3.1.1 *alarm rule, n*—user-selectable detector 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 trace detector.

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 trace detector 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 a trace detector 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 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 a trace detector.

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 a trace detector.

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 *ion mobility spectrometry, IMS, n*—detection technology commonly used in commercial trace detectors.

3.1.11.1 *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.

3.1.12 *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.

3.1.12.1 *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 trace detector 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 detection thresholds in that system.

3.1.12.2 *Discussion*—LOD90 values are independent of

alarm thresholds. However, once the alarm thresholds are set, the amount of substance needed to consistently elicit an alarm is called the LOD-A (Practice E2520). A LOD-A value for a substance in a trace detector is greater than or equal to its LOD90 value.

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

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

3.1.15 *process blank, n—see* blank.

3.1.16 *reference swabs, n—see* swabs.

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

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

3.1.18 *substrates, n—see* swabs.

3.1.19 *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.

3.1.19.1 *Discussion*—Distributed by instrument manufacturers and consumable suppliers, swabs have particular properties and shapes designed to fit into the sampling inlets of trace detectors. 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.

3.1.20 *swipe media, n—see* swabs.

3.1.21 *trace detector, n*—device used to identify the presence of particular analytes, with sensitivity allowing detection of less than one microgram of substance.

3.1.21.1 *Discussion*—Trace detectors may be set in general or specific modes of detection, where firmware allows optimization of operational conditions for explosives or drug detection. In airports for example, trace detectors are commonly set for explosives-only detection, whereas in prisons they are optimized for detection of certain drugs of interest.

3.1.21.2 *Discussion*—Explosive trace detectors are commonly known as ETDs. Trace detectors for explosives and drugs have been called contraband trace detectors and illicit drug-ETDs, but these names are imprecise and introduce unnecessary legal definitions to the types of substances detected.

3.1.22 *traps, n—see* swabs.

3.1.23 *wipes, n—see* swabs.

4. Summary of Test Method

4.1 Prepare reference solutions containing known concentrations of a particular analyte.

4.2 Set standard operating conditions for the trace detector. If needed, the target analyte is programmed into the database.

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

4.4 Assure that the trace detector is in operational readiness.

4.5 Perform exploratory measurements 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, prepare four mass levels of reference swabs that provide appropriate bracketing of the estimated LOD90 value.

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

4.8 Evaluate data using the web-based calculator at https://www-s.nist.gov/loda. This process returns an estimate of the LOD90 value as well as upper confidence and tolerance limits. Options include data plotting and outlier tests. The alpha and beta risks may be changed from the default values.

4.9 Consider guidance regarding the setting of an alarm threshold in the tested trace detector to achieve a reliable balance of alpha and beta risks.

5. Significance and Use

5.1 Commercial trace detectors are used by first responders, security screeners, the military, and law enforcement to detect and identify explosive threats and drugs of interest quickly. These trace detectors 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. A trace detector 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 The LOD for a substance is commonly accepted as the smallest amount of that substance that can be reliably detected in a given type of medium by a specific measurement process (**2**). 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 but pitfalls exist in specific applications. Vendors of trace detectors often report detection limits for only a single compound without defining the meaning of terms or reference to the method of determination.

NOTE 2—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, the limit of quantitation, and the minimum consistently detectable amount. 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, the individual performance of a trace detector (for example, realistic LODs) is influenced by: (*1*) manufacturing differences, history, and maintenance; (*2*) 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 a trace detector may be poorly estimated by the factory specifications. These fundamental measures of performance are critically important for assessing the ability of an instrument to detect trace levels of particular compounds in a particular setting, so a reliable and accessible method is needed to estimate realistic LOD values, especially in the field.

5.4 *Technical Challenges and Pitfalls to the Estimation of LOD Values in Trace Detectors and the Setting of Optimal Alarm Thresholds:*

5.4.1 *Scope*—The U.S. Department of Justice lists over 230 explosive materials and over 270 controlled drugs having a high potential for abuse.[4] There are many technologies used for trace detection, and instrument 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 detector performance. Therefore, default 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 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 a trace detector may not be adequate for the deployment situation.

5.4.4 *Signal Variability (Heteroskedasticity)*—The variance in instrument response may not be consistent across analyte mass levels introduced into the trace detector. 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 response regions. Typical methods of LOD estimation 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 trace detectors 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 trace detectors may be based on multiple-peak responses rather than a single-peak amplitude measurement. 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 trace detectors and technologies 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 trace detectors may not be openly published because of security and classification issues.

6. Apparatus

6.1 Dispensing device calibrated to deliver 1.00-µL aliquots.

6.2 Trace detector in operational readiness.

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 trace detector.
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 trace detector. While not ordinarily considered a hazard, the user should also be aware that many trace detectors 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 Prepare reference swabs containing the analyte at known levels within the sweet spot with a deposition uncertainty of less than 5 %. For this purpose, carefully prepare and dispense 1.00-µL aliquots of reference solutions onto the swabs using a calibrated pipette. 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.

NOTE 3—A few organizations use drop-on-demand inkjet printing for accurate and precise deposition of trace analytes, but these dispensing systems are not widely available.

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

NOTE 4—Calibrations of volumetric flasks and pipettes are not specifically covered in this test method, but guidance and procedures are

[4] A list of controlled drugs is available from https://www.deadiversion.usdoj.gov/schedules/orangebook/e_cs_sched.pdf.