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.

9.2.1.6 *Solution F*—1.00 ng/µL.
9.2.1.7 *Solution G*—3.00 ng/µL.
9.2.1.8 *Solution H*—10.0 ng/µL.
9.2.1.9 *Solution I*—30.0 ng/µL.
9.2.1.10 *Solution J*—100 ng/µL.

9.2.2 As a source of analyte, we recommend the use of certified solutions from a reliable chemical supplier. These solutions are usually sold in 2-mL ampoules with a nominal concentration of 1 mg/mL. Diluting 1.00 mL of this certified solution to 10 mL results in Solution J. The other analyte solutions may then be derived from Solution J, for example:

9.2.2.1 Solution J, 3 mL, diluted to 10 mL gives Solution I;
9.2.2.2 Solution J, 1 mL, diluted to 10 mL gives Solution H;
9.2.2.3 Solution I, 1 mL, diluted to 10 mL gives Solution G;
9.2.2.4 Solution H, 1 mL, diluted to 10 mL gives Solution F;
9.2.2.5 Solution G, 1 mL, diluted to 10 mL gives Solution E;
9.2.2.6 Solution F, 1 mL, diluted to 10 mL gives Solution D;
9.2.2.7 Solution E, 1 mL, diluted to 10 mL gives Solution C;
9.2.2.8 Solution D, 1 mL, diluted to 10 mL gives Solution B; and
9.2.2.9 Use pure solvent as Solution A.

9.2.3 Aliquots of these solutions should be transferred to labeled 10-mL vials with tight caps. After determining the most useful concentrations (9.7 and 9.8), these particular solutions may be transferred and stored for later use in 1-mL amber gas chromatographic (GC) vials with tight caps; crimped lids or vials flame sealed under an inert gas are preferred. To aid stability, all solutions should be stored at a temperature between 0 to 10°C and should be used at room temperature.

9.3 *Set Standard Operating Conditions*—The LOD90 value for any analyte will be dependent on the ETD operating conditions, so these conditions shall be set for the determination. Optimal conditions are rarely known, so we recommend using the "default" conditions formulated by the ETD manufacturer that balance performance across a wide variety of compounds. If the target analyte has been pre-programmed into the ETD, continue to 9.5; if not, the analyte shall be programmed into the ETD (see 9.4).

9.4 *Program Target Analyte into ETD*—If the target analyte is not programmed in the ETD, this may be done by adding the new substance characteristics into the ETD database according to the manufacturer's instructions. The manufacturer should be consulted regarding the viability of the addition because of possible interferences and other practical detection issues. If viable, programming will involve preparing several reference swabs containing the new substance and running these swabs on the ETD to identify the analyte peak position and other characteristics. This process may be carried out in 9.7, in which the amounts of analyte introduced to the ETD are varied until significant signals are obtained. These signals may be used to program the new analyte into the ETD.

9.5 *Precondition Swabs with "Chemical Background" (Optional)*—Clean swabs may be preconditioned using any reproducible method that introduces low levels of chemical background. The methods of preconditioning are at the discretion of the user but should provide a realistic example of deployment conditions. This may involve exposing the swabs to high humidity or room dust, swiping a nearby surface expected to be free of contraband residues, or depositing doses of an interferent/suppressant material onto the sweet spot of the swab. In any case, swabs should be treated consistently.

9.6 *ETD Operational Readiness*—Before starting, the ETD shall be in operational readiness, that is, up to date on maintenance, calibrated, and "conditioned." The performance of highly sensitive detectors, and especially ETDs, may be affected by trace vapor adsorption in the inlet. Typically, the first several analyses of reference swabs may show variations in ETD response, so it is important to "condition" the ETD in a realistic way that will enable statistical control of ETD performance and allow this method to determine an accurate LOD90 estimate. We recommend conditioning the ETD with a few reference swabs dosed at 10 ng of the target analyte, then running several process blanks to clear down the signal before starting any analysis sequence (Practice E2520).

9.7 *Exploratory Measurements*—The approximate LOD shall be determined to design an optimal measurement sequence without requiring undue measurements or overloading the ETD with excessive analyte. Essentially, the lowest mass level of analyte shall be identified that gives quantitative responses significantly greater than those from process blanks. This mass level will be called the significant mass level (SML). The SML may or may not elicit an alarm from the pre-programmed alarm rules, so alarms should be ignored (or turned off) at this stage. Start by preparing five reference swabs each at the 0.0-ng (process blank) and 0.3-ng levels by depositing 1 µL of the appropriate reference solutions onto the sweet spot of clean (or pretreated) swabs and allowing the spots to dry completely. After drying, run the process blanks and the 0.3-ng reference swabs on the ETD. Assuming the ETD has been factory programmed for the analyte, look for signals in the appropriate channel(s). Each channel used in the alarm rule for the particular analyte must be monitored. Note the quantitative signals (if any) for the process blanks and compare with the signals (if any) for the 0.3-ng reference swabs. If needed, perform a two-sided *t*-test at the 95 % confidence level **(10)** to determine whether a significant difference exists between the means of the responses and then follow the appropriate procedure in 9.7.1 and 9.7.2 to identify the SML. Because of signal processing and truncation, many responses may be absent (null). These should be designated as "zeroes." ETD responses at the SML level shall not contain any zeroes.

9.7.1 *Case 1 (Mean Responses Not Statistically Different, or Null Responses Evident at 0.3 ng)*—Prepare five reference swabs at the 1-ng level and compare these responses with those from the prior process blanks. If these mean responses are also not statistically different, or null responses are evident at 1 ng, continue running higher and higher mass levels until the mean responses of the process blanks and reference swabs are statistically different. The SML will be the lowest mass level that gives a statistically significant different response from the process blanks and each replicate gives a non-zero response.

9.7.2 *Case 2 (Mean Responses are Statistically Different)*—Prepare five reference swabs at the 0.1-ng level and compare these responses with those from the prior process blanks. If these mean responses are also statistically different, continue

running lower and lower mass levels until the mean responses of the process blanks and reference swabs are not statistically different. The SML will be the lowest mass level that gives a statistically significant different response from the process blanks, and each replicate gives a non-zero response.

9.8 *Prepare Reference Swabs for LOD90 Determination*—The LOD90 value will likely be nearer to the SML than any other prepared mass level. Since each mass level is about a factor of three apart, there is considerable range in which the LOD90 value may reside. The statistical method works best when mass levels are chosen that closely bracket the true LOD90 value. The experimental design, therefore, uses the SML to anchor the formulation of four appropriate mass levels derived from the solutions prepared.

9.8.1 *Prepare Reference Swabs Across Four Mass Levels*—There are two cases to consider: Case 1—when 90 % or more (here, five out of five) of the process blanks give null responses and Case 2—when more than 10 % of the process blanks (here, at least one of five) give non-zero responses. The cases differ only in the lowest amount of analyte tested. We define Soln(SML) as the solution for which a 1-µL aliquot gives the SML response and Soln(SML-1) as the solution at the next lower concentration. So, for example, if the SML = 10 ng, then Soln-H = Soln(SML) and Soln-G = Soln(SML-1).

9.8.1.1 *Case 1*—Deposit and evaporate (at room temperature) replicates of the following solution volumes onto 12 clean (or preconditioned) swabs. Be sure that the solutions are deposited on the swabs' sweet spot and that the fluid does not wick or spread outside a 0.5-cm diameter circle. This procedure will ultimately result in 48 samples (see Table 1).

9.8.1.2 *Case 2*—Deposit and evaporate (at room temperature) replicates of the following solution volumes onto 12 clean or preconditioned swabs. Be sure that the solutions are deposited on the swabs' sweet spot and that the fluid does not wick or spread outside a 0.5-cm diameter circle. This procedure will ultimately result in 48 samples (see Table 2).

(1) Depending on Level 1 results, there may be a requirement to prepare additional process blank samples to characterize the background response better. This requirement would be transmitted to the user of the web calculator (Section 10).

9.9 *Analyses*—Assure that the ETD is in operational readiness (9.6). Sequentially run all twelve of the samples prepared at Level 1. Between each sample, run a clean blank substrate until the channel clears. Record the dose level and numerical response, even if that response is "zero." Repeat with the twelve Level 2 samples and continue up through Level 4.

10. Data Evaluation

10.1 Data are evaluated using the web-based tool at http://pubapps.nist.gov/loda. Data are input by the user, and a LOD90 value (with associated upper confidence and tolerance limits) is determined for the analyte in the ETD response channel considered. The evaluation method is summaraized in 10.2.

TABLE 1 Case 1

Reference Swabs	Reference Solution	Number of 1-µL Aliquots
Level 4	Soln(SML)	2
Level 3	Soln(SML)	1
Level 2	Soln(SML-1)	2
Level 1	Soln(SML-1)	1

TABLE 2 Case 2

Reference Swabs	Reference Solution	Number of 1-µL Aliquots
Level 4	Soln(SML)	2
Level 3	Soln(SML)	1
Level 2	Soln(SML-1)	2
Level 1	Soln-A (blank)	1

10.2 *Summary of Data Evaluation Method:*

10.2.1 A truncated normal distribution model is used to obtain a value and uncertainty for LOD90 in the ETD channel considered. Here, a non-negative threshold terminus is estimated that makes positive readings possible only if the underlying Guassian-distributed amplitude is above this terminus. The model incorporates four additional parameters: the slope and the intercept of the regression, the background noise, and the error variances. LOD90 is a function of these parameters, and statistical theory is used to estimate this value along with the uncertainty. The default alpha and beta risks are each set at 10 %, although these can be changed to suit the application. The upper confidence limit and the tolerance estimates are also derived (**11**, **12**). Further details may be found in Ref **13**.

10.2.2 Minimum data requirements include ten replicated measurements at two dosing levels bracketing the LOD90 level, as well as ten process blank measurements. There is a benefit in minimizing the bracket distance, but this requires foreknowledge of the LOD90 target dosage. There is also a benefit in performing more than ten replications per level. There may be instances when the method fails to return a LOD90 value because data quality cannot support the LOD90 definition. In such cases, the method will return a reason and solution to the problem.

11. Guidance Regarding Appropriate Use and Application of LOD90

11.1 *Peak Detection Threshold Settings and Alpha and Beta Risk Levels:*

11.1.1 It is recommended that each channel detection threshold pertinent to an analyte in a particular ETD be set to a signal level called the critical value (CV). The CV is an available option returned from the web calculator. If an ETD is so programmed with realistic critical values (that is, determined with realistic process blanks), the following may be stated regarding the resulting alpha and beta risk levels.

11.1.1.1 The probability of any detection alarm when a sample contains no targeted analytes will be 10 % or less (alpha risk <10 %).

11.1.1.2 For analytes with alarm rules that use single-channel detection, the probability of a non-alarm when the analyte is present at its LOD90 level (or above) will be 10 % or less (beta risk <10 %).

11.1.1.3 For analytes with alarm rules requiring multiple channel detection, the probability of a non-alarm will be 10 % when the analyte is present at the highest LOD90 level needed

among the multiple channels required for detection. However, multivariate issues may apply **(14)**.

11.1.2 In this test method, a procedure is described for determining practical LOD90 values with alpha and beta detection risks set at 10 % and below for an ETD system operated in a particular location and a fixed configuration. Depending on circumstances, knowledge of LOD values with associated alpha and beta detection risks different from the default values may be required. These may usually be determined with the same data by simply changing the risk and confidence levels in the optional settings of the web calculator, although it is possible the algorithm will then require measurement data from an additional mass level.

12. Precision and Bias[5]

12.1 Metrics of precision and bias (JCGM 100:2008, Terminology E456, and Practice E177) were determined by an interlaboratory study (Practice E691) in which each of ten independent participants in eight laboratories tested two same-model detectors on three separate days using one common analyte (an explosive simulant) distributed at nine different concentrations, including blanks. Four different models of commercial IMS detectors were involved, as well as a gas chromatography/mass spectrometry (GC-MS) instrument. Operating configurations were typically set to the optimized "factory default" settings, but these were not common across the different models. These factory settings were generally formulated for explosive compounds so they were likely not optimized for the nonexplosive analyte; therefore, the precision values determined here are considered conservative. Data were evaluated using a standard NIST package for determination of consensus means **(13)** as detailed in the associated ASTM Research Report No. E54-1000.[5]

12.2 Based on the results of this study, the following criteria are recommended for judging the acceptability of results (Guides E1323 and E2655).

12.2.1 *Single-Laboratory, Single-Instrument Repeatability*—The median standard deviation of LOD90 results, obtained by the same analyst on the same instrument on different days, is estimated at 2.3 ng (34 % relative standard deviation) for n = 20. LOD90 values are considered suspect (95 % confidence level) if their standard deviations are greater than 12 ng and their relative standard deviations (RSDs) are greater than 70 %.

12.2.2 *Single-Laboratory, Matched-Instrument Repeatability*—The median average difference in LOD90 results, obtained by the same analyst on two different (but same-model) instruments, is estimated at 2.2 ng for n = 10. Given that this result is within the single-instrument repeatability, this suggests that same-model instruments should give nearly equivalent LOD90 results within a single laboratory. This was the case in this exercise because the instruments had similar operational histories within each laboratory. Since this may not always be the case (see 12.2.3), we do not recommend that this metric be used to judge the acceptability of results but rather used as a metric of performance across two or more ETDs using a common analyte.

12.2.3 *Multi-Laboratory, Matched-Instrument Reproducibility*—Three models of ETDs were used by multiple laboratories. For each model, the average difference in the multi-laboratory LOD90 values obtained was 2.0 ng (ETD Group Y, n = 3), 4.9 ng (ETD Group W, n = 3), and 97.8 ng (ETD Group Z, n = 2); the standard deviations of the LOD90 values were 1.7, 8.7, and 10.8 ng, respectively. We can conclude from these results that matched instruments in different laboratories usually have different operational histories and, therefore, statistically distinct LOD90 values.

12.2.4 *Multi-Laboratory, Multi-Instrument Reproducibility*—The standard deviation of all LOD90 values obtained by different independent analysts on different instruments is estimated as 35.5 ng (n = 32), while the range in the LOD90 values obtained covers almost four orders of magnitude. This result was expected from the diversity of detectors used in this exercise and the fact they were optimized for explosives rather than the non-explosive analyte.

12.3 *Bias*—Bias is difficult to estimate accurately since the LOD90 values determined are fundamental to each analysis system, which includes the distinctive history, operational settings, and deployment conditions of the detector. There is no definitively known LOD90 for any practical ETD system. However, the test method does provide upper tolerance bounds for each LOD90 estimate, which is a measure of potential bias from sources related to the ETD response model and statistical variations of the data. These tolerance bounds closely bracket the day-to-day variations in LOD90 values observed within laboratories so are considered apt estimates of bias from Type A error sources (see 12.2.1). Type B evaluation of error could not be performed, which considers biases in user inputs. These biases may arise from systematic uncertainties in the dispensed volumes to produce reference swabs (Specification E1154) or drifts in instrumental response (lack of adequate statistical control). Other possible systematic biases may derive from uncertainties in the concentrations and stabilities of the stock and reference solutions. These were insignificant in the interlaboratory exercise but should be considered when working with less-stable chemical analytes.

13. Keywords

13.1 alarms; detection; explosives; limit of detection; LOD90; risks; screening; swabs; thresholds; trace; uncertainty

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E54-1000. Contact ASTM Customer Service at service@astm.org.

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