Performance Validation for Explosive Trace Detection

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Outline

• Trace detection and challenges
• Role of metrology and standards
• Inkjet printing, ASTM limit of detection, cloud computing, and standard dirt
Trace detection involves quantities of substance invisible to the unaided eye... typically less than a microgram.

Most commercial explosive trace detectors (ETDs) can detect in the low nanogram range (a single crystal much smaller than the width of a human hair!)
Trace Detection Challenges: Sampling

Trace chemical targets are vanishingly small

RDX crystals in C4


20 parts per quadrillion


2 parts per billion
Trace Detection Challenges: Specificity/Sensitivity

Contamination is ubiquitous, compositionally variable, and can interfere with detection
ETD Response Curves

Vendor-supplied test materials

Maximum amplitude (a.u.)

Analyte mass (ng)
Ink Jet Printing
Inkjet Metrology and Application to Trace Explosive Validation

**Inkjet Metrology: High-Accuracy Mass Measurements of Microdroplets Produced by a Drop-on-Demand Dispenser**

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We describe gravimetric methods for measuring the mass of droplets generated by a drop-on-demand (DOD) microdispenser. Droplets are deposited, either continuously at a known frequency or as a burst of known number, into a cylinder positioned on a submicrogram balance. Mass measurements are acquired precisely by computer, and results are corrected for evaporation. Capabilities are demonstrated using indium-tin oxide droplets. For ejection rates greater than 100 Hz, the reproducibility of droplet mass measurements was 0.2%, while the combined relative standard uncertainty (u_r) was 0.9%. When bursts of droplets are dispensed, the limit of quantification was 72 μg (1,400 droplets) with u_r = 1.0%. Individual droplet size in a burst was evaluated by high-speed videography. Dimensions were consistent from the tenth droplet onward, and the mass of an individual droplet was best estimated by the average droplet mass with a combined uncertainty of about 1%. Diameters of the first several droplets were anomalous, but their contribution was accounted for when dispensing bursts. Above the limits of quantification, the gravimetric method is rapid and precisely measures droplet mass and average size.

**Application of Inkjet Printing Technology to Produce Test Materials of 1,3,5-Trinitro-1,3,5-Triazacyclohexane for Trace Explosive Analysis**

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The feasibility of using piezoelectric drop-on-demand inkjet printing to produce test materials for trace explosive analysis is demonstrated. RDX, (1,3,5-trinitro-1,3,5-triazacyclohexane) was formed into inkjet printable solutions and jetted onto substrates suitable for calibration of the low mobility spectrometry (LMS) instruments currently deployed worldwide for contraband screening. Gravimetric analysis, gas chromatography/mass spectrometry (GC/MS), and ultraviolet-visible (UV−vis) absorption spectroscopy were used to verify inkjet printer solution concentrations and the quantity of explosive dispensed onto test materials. Reproducibility of the inkjet printing process was validated by mass deposition of the explosive RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) was determined to be better than 2% for a single day of printing and better than 3% day to day.

With the threat of global terrorism on the rise, the ability to detect trace levels of explosives has become an issue of critical national importance. This is especially true for screening locations including airports, seaports, U.S. embassies, and other government facilities. Gravimetric techniques have been used for explosive detection in a variety of applications, including explosives detection in luggage, personal belongings, and vehicles. The combined standard uncertainty of the method has been demonstrated to be less than 1% (k=1). This study demonstrates the feasibility of using inkjet printing technology to produce test materials for trace explosive analysis.

**Inkjet Metrology II: Resolved Effects of Ejection Frequency, Fluidic Pressure, and Droplet Number on Reproducible Drop-on-Demand Dispensing**

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In a typical screening implementation, personnel screen baggage or cargo surfaces such as baggage handles or package labels with a "trip" composed of cloth, paper, or polytetrafluoroethylene (PTFE) coated material. Interviewed as administered the unwrapped is vaporized vapor is then ionized via electron impact ionization, thus their atmosphere time-of-flight drift tube configuration, and the library of known test mate is typically not calibrated for proper identification of known materials as test materials. In this study, we report on the effects of ejection frequency, fluidic pressure, and droplet number on reproducible drop-on-demand dispensing.
Production of Test Materials Using Ink Jet Printing

MicroFab Gravimetric Printer (JL4-XLB)

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy</td>
<td>5 %</td>
</tr>
<tr>
<td>Repeatability</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Deposition Range (&lt;1 min)</td>
<td>1 pg to 1 µg</td>
</tr>
<tr>
<td></td>
<td>70 pL to 70 µL</td>
</tr>
<tr>
<td>Spatial Resolution</td>
<td>100 µm</td>
</tr>
</tbody>
</table>
ASTM Limit of Detection & Cloud Computing
ASTM E54.01 Proposed Standard on Limit of Detection for ETDs

L_D: a fundamental yet misunderstood analytical metric

We define the L_D-90 as the lowest mass of a particular compound – introduced to the sampling inlet of a well-functioning contraband detection system – for which 90 % of independent measurements result in true detection, while the true non-detection probability is at least 90 % when measuring independent process blank samples.

L_D-90 influenced by combination of detector sensitivity, response repeatability, and specificity for the analyte against background interferences.

http://www.chemometry.com/Research/LOD.html
LOD Method for ETDs

NIST method designed specifically for trace explosive detectors as implemented by ASTM E54.01 subtask group*


* S. Leigh, A. Rukhin, J. Yen, J. Staymates, M. Verkouteren
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimator</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>( \hat{a}, \bar{a} )</td>
<td>Intercept of response ( W )</td>
</tr>
<tr>
<td>( b )</td>
<td>( \hat{b}, \bar{b} )</td>
<td>Slope of response ( W )</td>
</tr>
<tr>
<td>( \sigma_0^2 )</td>
<td>( \hat{\sigma}_0^2, \bar{\sigma}_0^2, \sigma_0^2 )</td>
<td>Error variance, blank sample</td>
</tr>
<tr>
<td>( \sigma^2 )</td>
<td>( \hat{\sigma}^2, \bar{\sigma}^2 )</td>
<td>Error variance, non-blank sample</td>
</tr>
<tr>
<td>( h )</td>
<td>( \hat{h}, \bar{h} )</td>
<td>Truncation parameter</td>
</tr>
<tr>
<td>( z_* = (h-a)/\sigma_0 )</td>
<td>( \bar{z}_* )</td>
<td>Percentile of ( Y(0) ) distribution</td>
</tr>
<tr>
<td>( LOD = x_c )</td>
<td>( LOD, \bar{LOD}, \hat{LOD} )</td>
<td>Limit of detection</td>
</tr>
<tr>
<td>( LC = \max(a+z_*-\alpha, 0, h) )</td>
<td>( \bar{L}C )</td>
<td>Critical level</td>
</tr>
<tr>
<td>( y_c = LC + z_1-\beta \sigma )</td>
<td>( \bar{y}_c )</td>
<td>Decision limit</td>
</tr>
</tbody>
</table>

\[
Y(x) = \begin{cases} 
0, & W(x) < h; \\
W(x), & W(x) \geq h. 
\end{cases} \tag{1}
\]

\[
\Pr(Y(0) \leq LC) = 1 - \alpha. \tag{2}
\]

\[
\Phi \left( \frac{h-a}{\sigma_0} \right) \prod_{j:y_j^0 > 0} \frac{1}{\sigma_0} \Phi \left( \frac{y_j^0-a}{\sigma_0} \right), \quad h \leq \min_{i:y_i^0 > 0} y_i^0. \tag{3}
\]

\[
\hat{h} = \min_{j:y_j^0 > 0} y_j^0. \tag{4}
\]

\[
\hat{\sigma}_0 = \frac{\bar{z}_* (\bar{y}_0 - \hat{h})}{2} + \sqrt{\left(1 + \frac{\hat{z}_*^2}{4} \right) (\bar{y}_0 - \hat{h})^2 + s_0^2}. \tag{5}
\]

\[
\hat{\sigma}_0 = \hat{\alpha} = \bar{h} - \hat{z}_* \hat{\sigma}_0. \tag{6}
\]

\[
\bar{h} = 2\hat{h} - \min_{j:y_j^0 > \hat{h}} y_j^0, \tag{7}
\]

\[
\bar{\sigma}_0 = \frac{\bar{z}_* (\bar{y}_0 - \bar{h})}{2} + \sqrt{\left(1 + \frac{\bar{z}_*^2}{4} \right) (\bar{y}_0 - \bar{h})^2 + s_0^2}. \tag{8}
\]

\[
\tilde{\sigma}_0 = \tilde{\alpha} = \bar{h} - \tilde{z}_* \tilde{\sigma}_0. \tag{9}
\]

\[
\phi = \frac{1}{\sqrt{\sum_i m_i x_i^2}}, \tag{10}
\]

\[
\hat{b} = d^2 \sum_i m_i x_i \bar{y}_i. \tag{11}
\]

\[
\hat{\sigma}^2 = \frac{1}{v} \sum_i \left( \bar{y}_i - \hat{b} x_i \right)^2. \tag{12}
\]

\[
\hat{LOD} = \frac{\max(z_{1-\alpha}, \bar{z}_*) \hat{\sigma}_0 + z_{1-\beta} \hat{\sigma}}{\hat{b}}. \tag{13}
\]

\[
\hat{\sigma}_0^2 = \frac{\max(z_{1-\alpha}, \bar{z}_*) \hat{\sigma}_0^2 + z_{1-\beta} \hat{\sigma}^2}{\hat{b}} \tag{14}
\]

\[
\hat{H} = \max(z_{1-\alpha}, \bar{z}_*) \hat{\sigma}_0 + z_{1-\beta} \hat{\sigma}. \tag{15}
\]

\[
\frac{t_{1-\gamma/2}(v)}{\sqrt{\sum_i m_i x_i^2}}. \tag{16}
\]

\[
U = \frac{\max(z_{1-\alpha}, \bar{z}_*) \hat{\sigma}_0 + (z_{1-\beta} + z_{1-\rho}) \hat{\sigma}}{\hat{b}}. \tag{17}
\]

Notation and Meaning:
- \( Y(x) \) Observable positive response at mass \( x \)
- \( W(x) \) Unobservable Gaussian response at mass \( x \)
- \( N \) Total number of samples (including blanks)
- \( n_0 \) Sample size of blanks
- \( m_0 \) Number of positive readings in the blank sample
- \( n_i \) Number of zero readings in the blank sample
- \( y_0 \) The sample mean of positive responses in the blank sample
- \( s_0^2 \) The sample variance of positive responses in the blank sample
- \( n_i \geq 1 \) Size of \( i \)-th non-blank sample
- \( m_i \geq 1 \) Number of positive readings in \( i \)-th non-blank sample
- \( d = 1/\sqrt{\sum_i m_i x_i^2} \) Defines confidence limit \( H \) for LOD
- \( \phi \) Standard normal density
- \( \Phi \) Normal cumulative distribution function
- \( z_\alpha \) Normal percentile of order \( \alpha \) \( \Phi(z_\alpha) = \alpha \)
Web-based LOD Calculator

  - Input measurement data
  - Data quality check
  - $L_D$-90 estimate & supporting information

ASTM Subtask Group:
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Standard Dirt
Standard “Dirts”
Natural Matrix NIST SRMs

- Soils, sediments, dusts, air particulates, sludges, leaves...
- Immediately and internationally available
- Represent reasonable contamination sources
- Highly characterized
- Certified
- Homogeneous
- Stabilized
Standard Interferent Material (SIMdirt-1)

SRM 2704 (Buffalo River Sediment) 266.5 mg
SRM 2585 (Household Dust)       83.7 mg
SRM 2709a (San Joaquin Soil)    87.5 mg
SRM 1650 (Diesel Particulate Matter) 5.1 mg
2-propanol (HPLC grade)         100 mL

One drop from squeeze dropper deposits 100 μg of SIMdirt-1 (U = 4%)
Limit of Detection Comparison

An atypical surprise with SIMdirt-1

Detector responses from analyte on clean substrates

Analyses repeated, with 100 μg SIMdirt-1 added to each substrate
SRM Preparers and Analysts

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Summary

• Several tools have been developed at NIST suitable for performance testing and validation of trace detectors
  
  • Inkjet technology for accurate and precise printing of pg-to-μg of compounds for reliable production of test materials and reference substrates
  
  • Proposed ASTM method for determining L_D-90, aided with a web-based calculator
  
  • Standard interferent material (SIMdirt-1) for ETD interference response testing

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