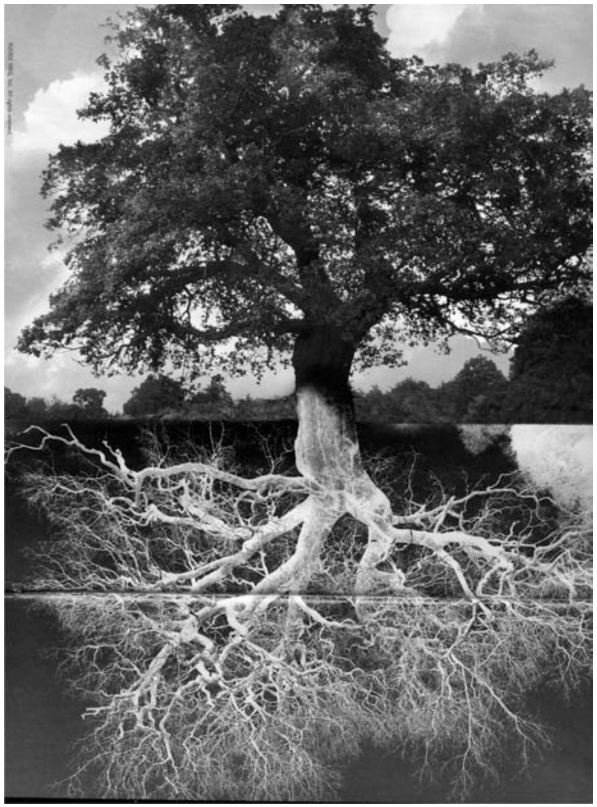
Performance Validation for Explosive Trace Detection



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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

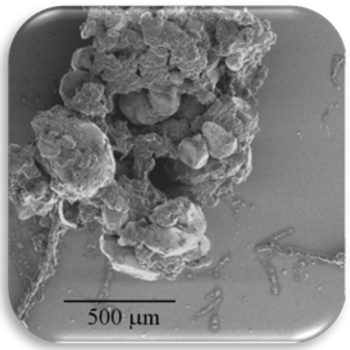
Trace Detection

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

+

http://showmehowto.net/wp-content/uploads/2012/07/788suitcase.jpg

=

20 parts per quadrillion

+

http://www.itstactical.com/centcom/news/youll-never-look-at-hay-bales-the-same/

=

2 parts per billion

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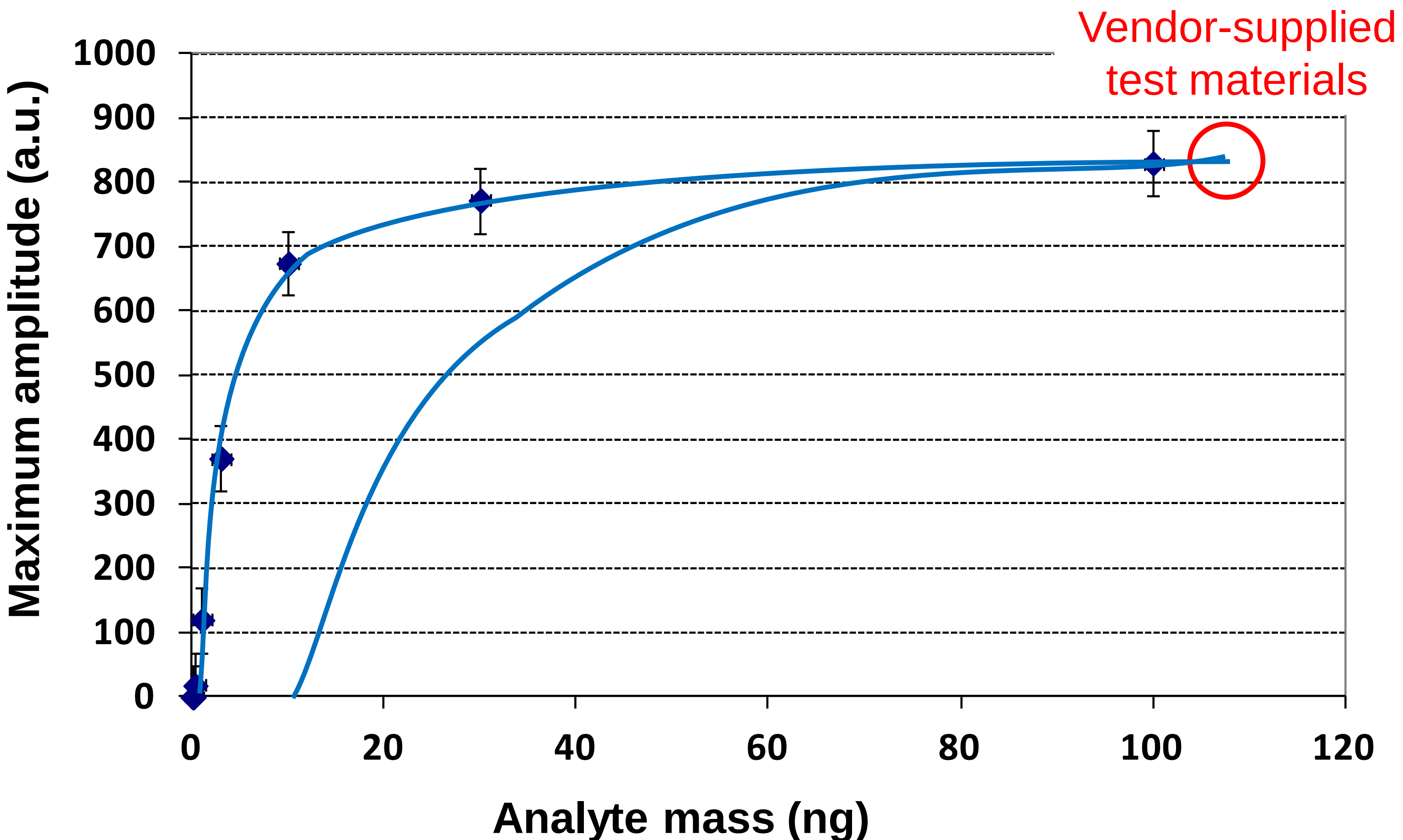
Trace Detection Challenges: Specificity/Sensitivity

Contamination is ubiquitous, compositionally variable, and can interfere with detection

ETD Response Curves



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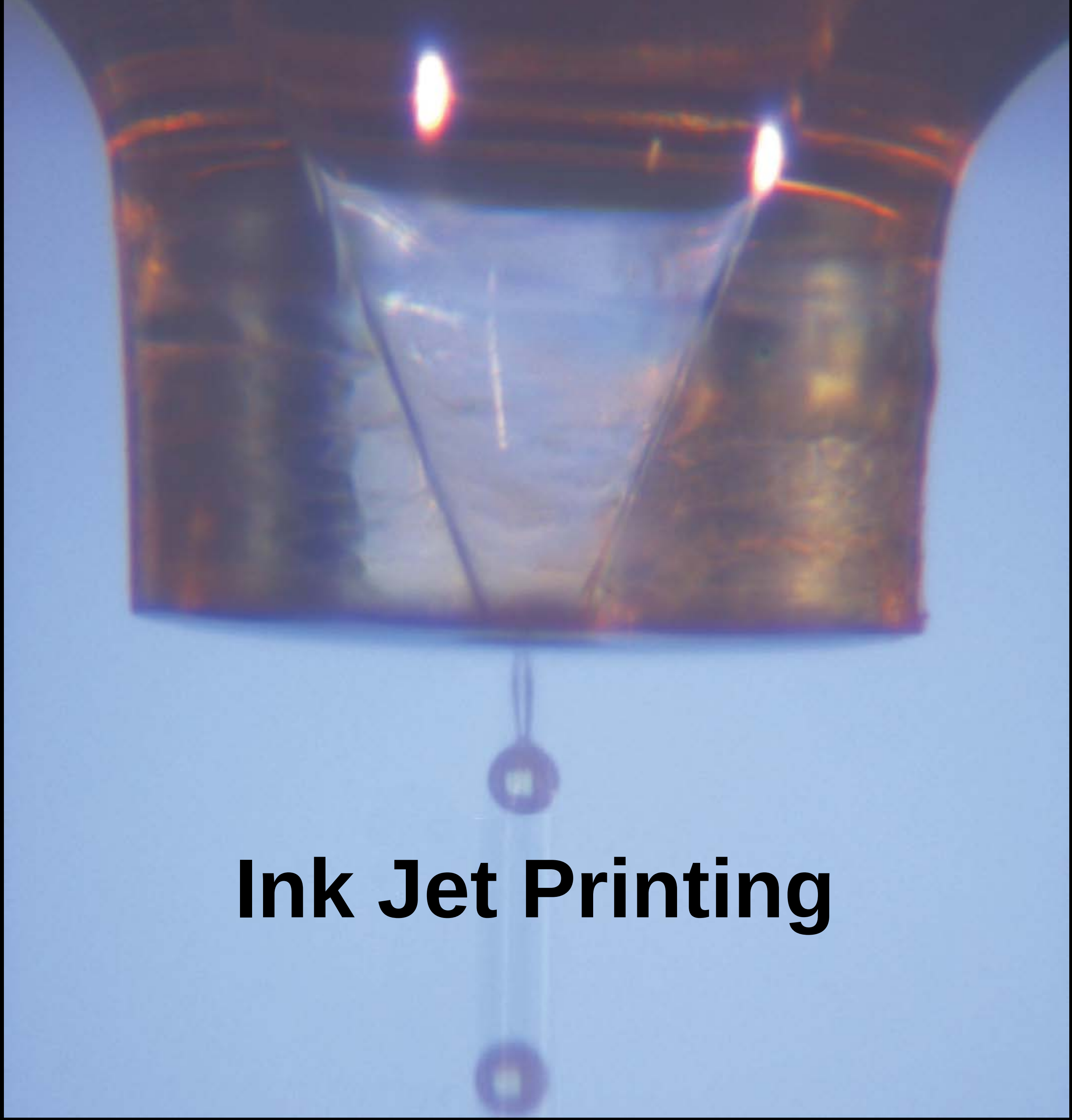
Ink Jet Printing



Inkjet Metrology and Application to Trace Explosive Validation

Anal Chem 2009, 81, 8577

Anal. Chem. **2009,** *81,* 8577–8584

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

R. Michael Verkouteren* and Jennifer R. Verkouteren

Surface and Microanalysis Research Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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 isobutyl alcohol droplets. For ejection rates greater than 100 Hz, the repeatability of droplet mass measurements was 0.2%, while the combined relative standard uncertainty (u_c) was 0.9%. When bursts of droplets were dispensed, the limit of quantitation was 72 μg (1490 droplets) with u_c = 1.0%. Individual droplet size in a burst was evaluated by high-speed videography. Diameters 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 quantitation, the gravimetric meth-

solder-based materials[9] require quantitative deposition and exact positioning of micrometer-sized "building blocks" to ensure reproducible feature size in partially and fully dense materials. Small volume dispense technologies are also used for precise and accurate delivery ... assays,[10–18] micr... devices,[20] olfactor... materials.[23] In lar... in these applicati... with determinati... aliquots. These ... operational and ... changes around ... delivery.

A rich and var... and droplet form...

(9) Lee, T.-M.; Kan... D.-S. *IEEE Tra*...
(10) Niles, W. D.; C...
(11) Bruns, A.; Hoff... 161–171.

Anal Chem 2010, 82, 8519

Anal. Chem. **2010,** *82,* 8519–8524

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

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The feasibility of the use of piezoelectric drop-on-demand inkjet printing to prepare test materials for trace explosive analysis is demonstrated. RDX (1,3,5-trinitro-1,3,5 triazcyclohexane) was formulated into inkjet printable solutions and jetted onto substrates suitable for calibration of the ion mobility spectrometry (IMS) 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 for mass deposition of the explosive RDX (1,3,5-trinitro-1,3,5 triazcyclohexane) 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 at screening locations including airports, seaports, U.S. embassies, and other government facilities. Although analytical techniques exist to detect quantitative...

In a typical screening implementation, personnel wipe baggage or cargo surfaces such as luggage handles or package labels with a "trap" composed of cloth, paper, or polytetrafluoroethylene (PTFE)-coated materials. Explosive particles are removed from the wiped sur... introduced int... are vaporized... vapor is then... ionized via ac... electron impa... roethane witl... ionization, th... their atmosp... time-of-flight... drift tube at c... charge, and t... library of kn...

Test mate... (typically nar... calibrating IM... properly at de... materials incl... large dynamic...

Langmuir 2011, 27, 9644

Langmuir ARTICLE

pubs.acs.org/Langmuir

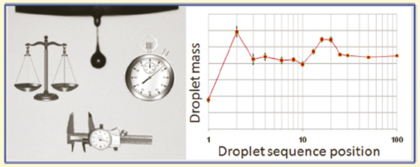
Inkjet Metrology II: Resolved Effects of Ejection Frequency, Fluidic Pressure, and Droplet Number on Reproducible Drop-on-Demand Dispensing

R. Michael Verkouteren* and Jennifer R. Verkouteren

Surface and Microanalysis Science Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

Supporting Information

ABSTRACT: We report highly reproducible gravimetric and optical measurements of microdroplets that lend insights into the fundamentals of drop-on-demand (DOD) printing. Baseline fluidic pressure within the DOD dispenser was controlled to within 0.02 hPa, enabling long-term stability in dispensed droplet mass with observed variations near 1% (RSD) for isobutanol. The gravimetric measurements were sensitive enough to detect and avoid unwanted effects from air bubbles within the dispenser. The gravimetric and optical velocity measurements enabled consistent determination of droplet



kinetic energy that governed baseline behavior across the operational variables. Mass and velocity were influenced in a nonlinear manner by the frequency of droplet ejection, the fluidic pressure within the dispensing device, and the number of droplets dispensed in a burst. Resolved effects were attributable to several possible mechanisms including acoustic resonances, energy partitioning from

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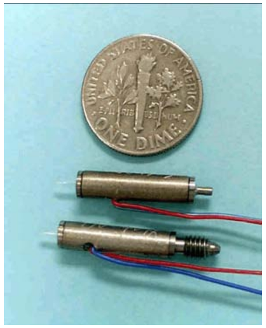
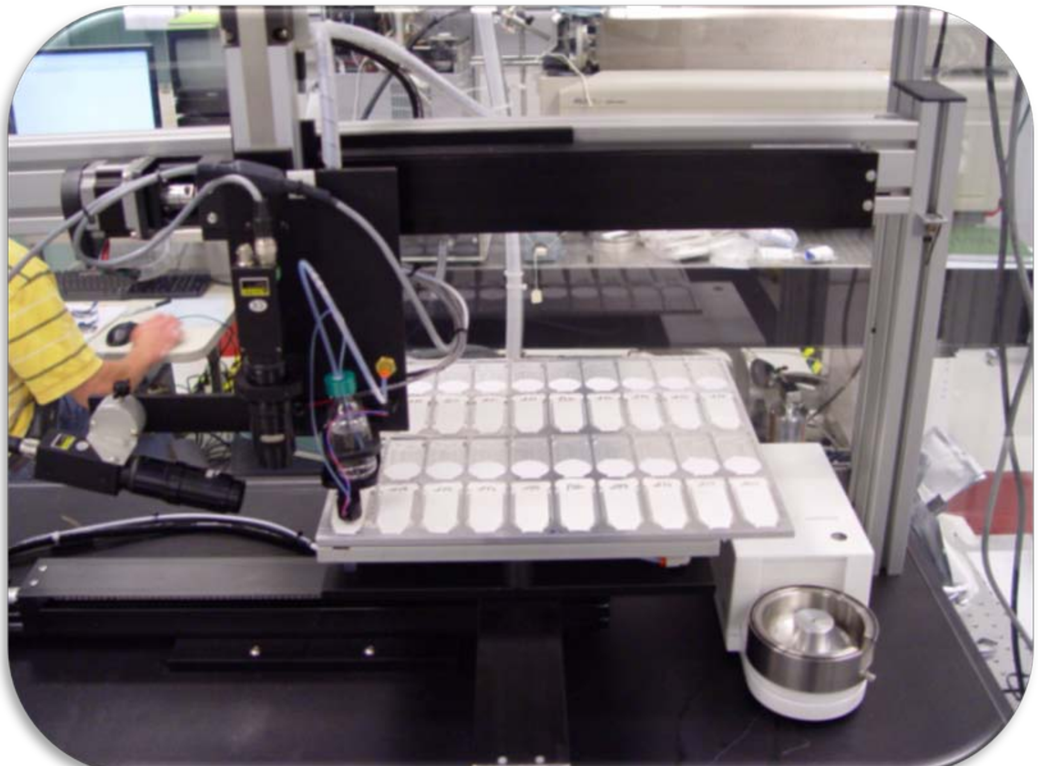
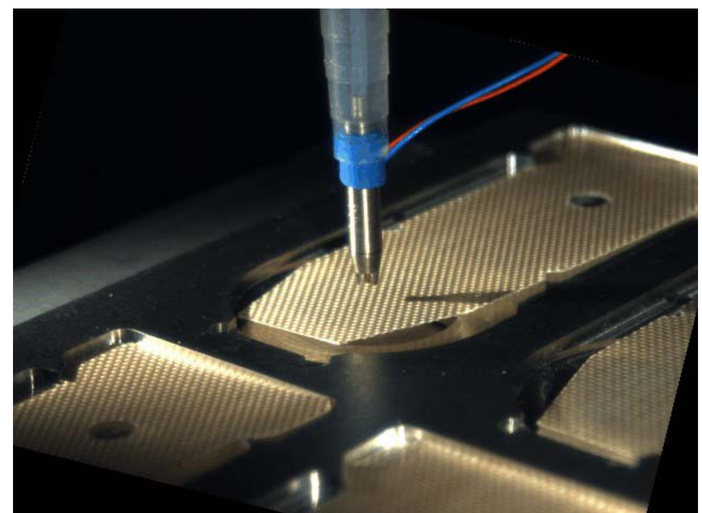


Production of Test Materials Using Ink Jet Printing

Accuracy	5 %
Repeatability	0.5 %
Deposition Range (<1 min)	1 pg to 1 µg 70 pL to 70 µL
Spatial Resolution	100 µm



MicroFab Gravimetric Printer (JL4-XLB)



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ASTM Limit of Detection
&
Cloud Computing

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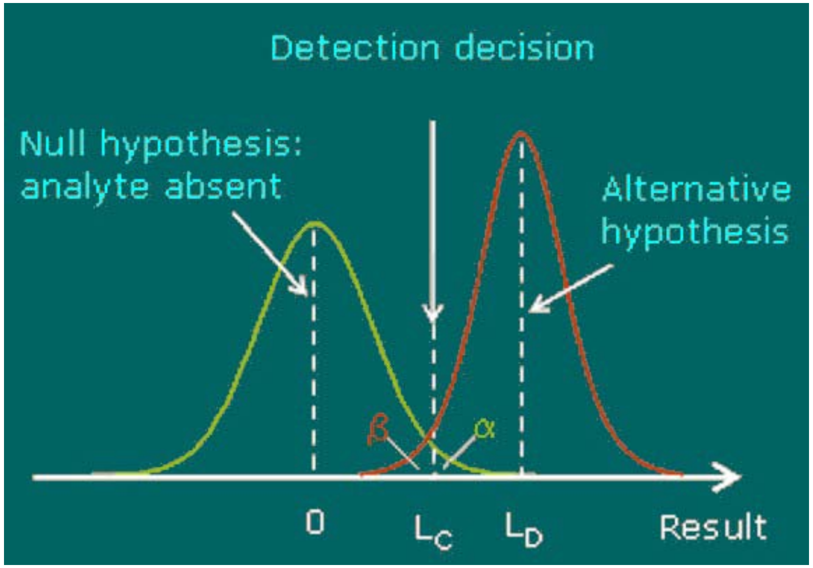
http://www.v3.co.uk/IMG/473/149473/cloud-computing-security-services-provider-370x229.jpg

ASTM E54.01 Proposed Standard on Limit of Detection for ETDs



http://www.chemometry.com/Research/LOD.html

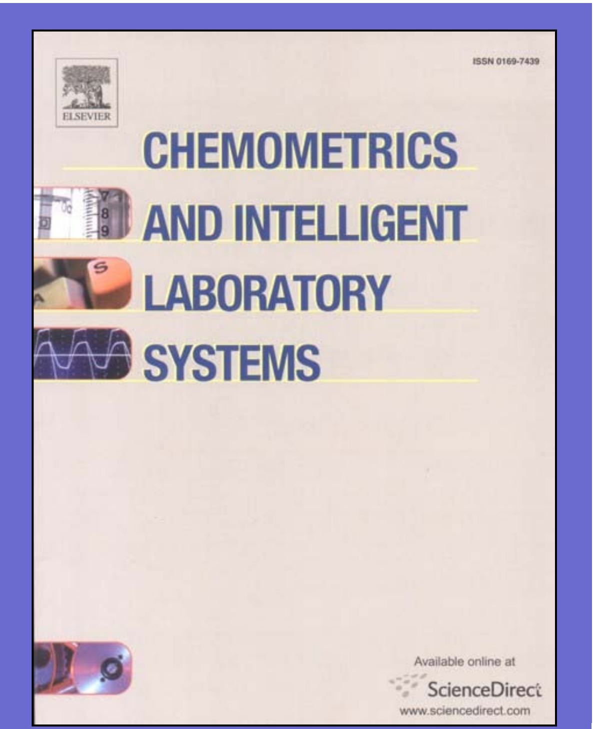
L_D: a fundamental yet misunderstood analytical metric

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.

LOD Method for ETDs

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



Limit of detection determination for censored samples. Rukhin, A.L.; Samarov, D.V. (2011) 105, 188-194.

* S. Leigh, A. Rukhin, J. Yen, J. Staymates, M. Verkouteren

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Parameter	Estimator	Definition
a	$\hat{a},\tilde{a}$	Intercept of response W
b	$\hat{b},\overline{b}$	Slope of response W
σ_0^2	$\hat{\sigma}_0^2,\tilde{\sigma}_0^2,\overline{\sigma}_0^2$	Error variance, blank sample
σ^2	$\hat{\sigma}^2,\overline{\sigma}^2$	Error variance, non-blank sample
h	$\hat{h},\tilde{h}$	Truncation parameter
$z_\star=(h-a)/\sigma_0$	$\overline{z}_\star$	Percentile of $Y(0)$ distribution
$\text{LOD}=x_c$ $=(\max(z_{1-\alpha},z_\star)\sigma_0+z_{1-\beta}\sigma)/b$	$\widehat{\text{LOD}},\widetilde{\text{LOD}}$, H,U	Limit of detection
$\text{LC}=\max(a+z_{1-\alpha}\sigma_0,h)$	$\widehat{\text{LC}}$	Critical level
$y_c=LC+z_{1-\beta}\sigma$		Decision limit

Notation	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
$\nu_0=n_0-m_0$	Number of zero readings in the blank sample
$\overline{y}_0$	The sample mean of positive responses in the blank sample
s_0^2	The sample variance of positive responses in the blank sample
$n_i, i\geq 1$	Size of i-th non-blank sample
$m_i, i\geq 1$	Number of positive readings in i-th non-blank sample
$\nu=\sum_{i=1}^N m_i-1$	Degrees of freedom
$d=1/\sqrt{\sum_i m_i x_i^2}$	Defines confidence limit H for LOD
ϕ	Standard normal density
Φ	Normal cumulative distribution function
z_α	Normal percentile of order $\alpha, \Phi(z_\alpha)=\alpha$

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

$$Pr(Y(0)\leq LC)=1-\alpha. \quad (2)$$

$$\Phi^{\nu_0}\left(\frac{h-a}{\sigma_0}\right)\prod_{j:y_j^{(0)}>0}\frac{1}{\sigma_0}\phi\left(\frac{y_j^{(0)}-a}{\sigma_0}\right),\ h\leq\min_{j:y_j^{(0)}>0}y_j^{(0)}. \quad (3)$$

$$\hat{h}=\min_{j:y_j^{(0)}>0}y_j^{(0)}. \quad (4)$$

$$\hat{\sigma}_0=\frac{\hat{z}_\star\left(\overline{y}_0-\hat{h}\right)}{2}+\sqrt{\left(1+\frac{\hat{z}_\star^2}{4}\right)\left(\overline{y}_0-\hat{h}\right)^2+s_0^2}. \quad (5)$$

$$\hat{a}=\hat{h}-\hat{z}_\star\hat{\sigma}_0. \quad (6)$$

$$\tilde{h}=2\hat{h}-\min_{j:y_j^{(0)}>\hat{h}}y_j^{(0)}, \quad (7)$$

$$\tilde{\sigma}_0=\frac{\hat{z}_\star\left(\overline{y}_0-\tilde{h}\right)}{2}+\sqrt{\left(1+\frac{\hat{z}_\star^2}{4}\right)\left(\overline{y}_0-\tilde{h}\right)^2+s_0^2}, \quad (8)$$

$$\tilde{a}=\tilde{h}-\hat{z}_\star\tilde{\sigma}_0. \quad (9)$$

$$d=\frac{1}{\sqrt{\sum_i m_i x_i^2}}, \quad (10)$$

$$\hat{b}=d^2\sum_i m_i x_i \overline{y}_i, \quad (11)$$

$$\hat{\sigma}^2=\frac{1}{\nu}\sum_{i,j}\left(\tilde{y}_j^{(i)}-\hat{b}x_i\right)^2. \quad (12)$$

$$\widehat{\text{LOD}}=\frac{\max(z_{1-\alpha},\hat{z}_\star)\tilde{\sigma}_0+z_{1-\beta}\hat{\sigma}}{\hat{b}}. \quad (13)$$

$$\widetilde{\text{Var}}\left(\widehat{\text{LOD}}\right)=\frac{1}{\hat{b}^2}\left[\left[\max(z_{1-\alpha},\hat{z}_\star)\right]^2\frac{\tilde{\sigma}_0^2}{m_0}+z_{1-\beta}^2\frac{\hat{\sigma}^2}{\nu}+d^2\hat{\sigma}^2\widehat{\text{LOD}}^2\right]. \quad (14)$$

$$H=\frac{\max(z_{1-\alpha},\overline{z}_\star)\overline{\sigma}_0+z_{1-\beta}\overline{\sigma}}{\overline{b}}, \quad (15)$$

$$\frac{\hat{b}}{\hat{\sigma}}>c=dt_{1-\gamma/2}(\nu)=\frac{t_{1-\gamma/2}(\nu)}{\sqrt{\sum_i m_i x_i^2}}. \quad (16)$$

$$U=\frac{\max(z_{1-\alpha},\overline{z}_\star)\overline{\sigma}_0+\left(z_{1-\beta}+z_{1-P}\right)\overline{\sigma}}{\overline{b}}. \quad (17)$$

Web-based LOD Calculator

- http://pubapps.nist.gov:8444/loda
  - Input measurement data

    ↓
  - *Data quality check*

    ↓
  - *L_D-90 estimate & supporting information*

ASTM Subtask Group:
A. Heckert,
K. Kwiatek,
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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

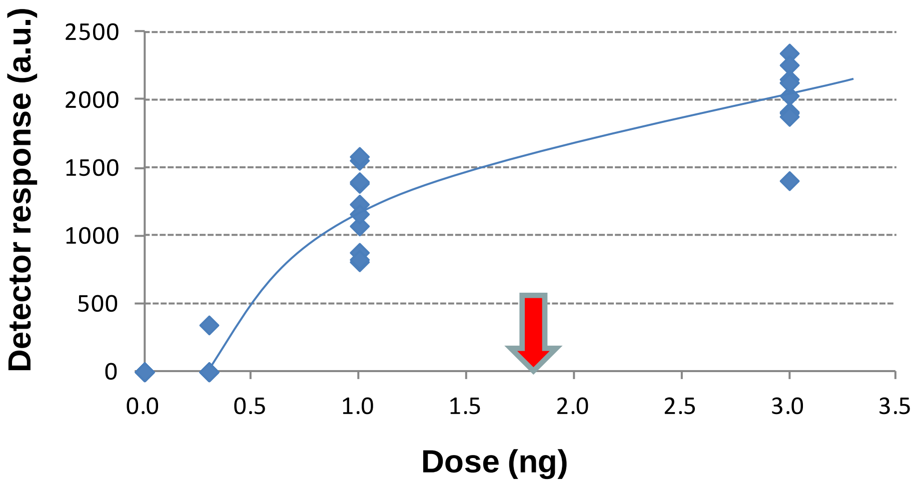
Standard Interferent Material (SIMdirt-1)

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

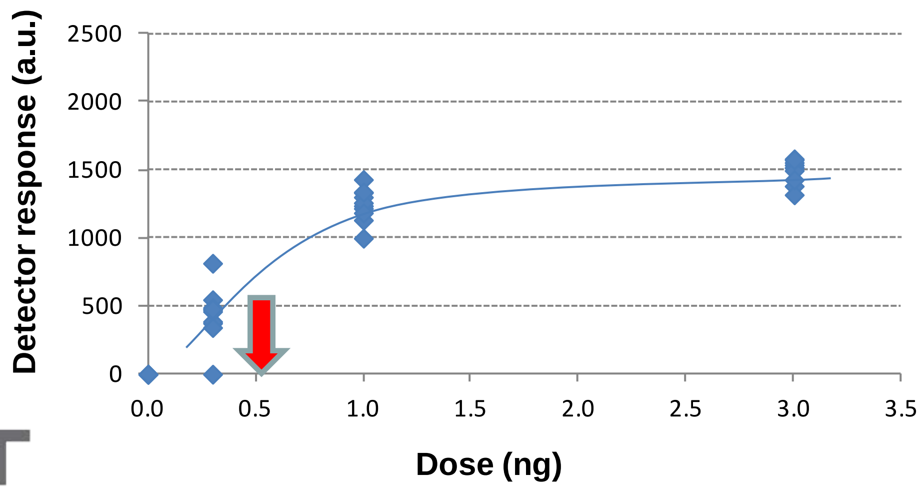
One drop from squeeze dropper deposits 100 µg of SIMdirt-1 (U = 4%)

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

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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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