Night Vision and Electronic Sensors Directorate

Reproducible Deposition of Trace Explosives Onto Surfaces for Test Standards Generation

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Fort Belvoir, Virginia 22060-5806

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By

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April 2010

Science and Technology Division
FORT BELVOIR, VIRGINIA 22060-5806

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE April 2010	3. REPORT TYPE AND DATES COVERED Monograph -December 2009

4. TITLE AND SUBTITLE

Reproducible Deposition of Trace Explosives Onto Surfaces for Test Standards Generation

5. FUNDING NUMBERS

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
US Army RDECOM CERDEC
Night Vision and Electronic Sensors Directorate
Fort Belvoir, VA 22060

8. PERFORMING ORGANIZATION REPORT NUMBER
RDER-NV-TR265

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

12b. DISTRIBUTION CODE

A

13. ABSTRACT *(Maximum 200 words)*
Best practice dictates that the performance metrics of an explosives-detecting sensor should be baselined against calibrated test samples under controlled conditions before testing proceeds to a rugged environment. This allows test parameters to be intelligently chosen for field testing, where the range of meaningful parameters would otherwise be too broad to allow efficient use of valuable field time. In support of internal field testing, the US Army RDECOM CERDEC Night Vision and Electronic Sensors Directorate (NVESD) has developed a technique which allows rapid generation of surfaces suitably dosed with explosive residues. The technique employs a commercial air spray gun to dispense controlled doses of dissolved analyte, requiring only relatively minor modifications. This approach was chosen with the vision of developing a method that would require minimal expense and effort to build. This monograph describes the process followed, and is compiled to serve as general guidance to sensor developers who wish to consider a similar approach.

14. SUBJECT TERMS
laser-induced breakdown spectroscopy (LIBS), Enhanced Spatial Homogeneity, TNT, Analyte Extraction Efficiencies, explosives and explosives-related compounds (EERCs).

15. NUMBER OF PAGES
12

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT None

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1 Introduction

Best practice dictates that the performance metrics of an explosives-detecting sensor should be baselined against calibrated test samples under controlled conditions before testing proceeds to a rugged environment. This allows test parameters to be intelligently chosen for field testing, where the range of meaningful parameters would otherwise be too broad to allow efficient use of valuable field time. When using calibrated test samples in the lab, judicious care must be taken to ensure that both sample preparation and presentation allow meaningful testing of sensor capabilities while simultaneously avoiding artifacts of the sampling process. Examples of sampling artifacts may be seen in laser-based approaches, where the interrogating beam samples only a small portion of any given surface. With laser-induced breakdown spectroscopy (LIBS), interrogation areas as small as a few millimeters in diameter are possible. In such instances any order-of-magnitude loading fluctuations occurring over similar length scales might lend great variance to signals already characterized by high sample-to-sample noise. Consequently, in developing point interrogation technologies for the standoff detection of explosives, a parallel need for the even deposition of thin, uniform analyte layers onto arbitrary substrates arises.

In support of internal field testing, the US Army RDECOM CERDEC Night Vision and Electronic Sensors Directorate (NVESD) has developed a technique which allows rapid generation of surfaces suitably dosed with explosive residues. The technique employs a commercial air spray gun to dispense controlled doses of dissolved analyte, requiring only relatively minor modifications. This approach was chosen with the vision of developing a method that would require minimal expense and effort to build. While the approach does not deliver the spatial precision hallmarked by more advanced deposition methods such as inkjet printing,[1,2] it provides excellent reproducibility (mass loading RSD ~ 5 %), high residue dispersion, high particle uniformity and rapid production rates for samples with mass loadings in the range of 0.1 to 20 µg/cm^2; material loadings typical of values reported in explosive residue studies.[3] This monograph describes the process followed, and is compiled to serve as general guidance to sensor developers who wish to consider a similar approach.

2 Experimental Overview

We describe below a means of topically dosing substrates with known, evenly-distributed quantities of explosives and explosives-related compounds (referred to collectively for here as EERCs). The resulting samples are designed to be suitable for the testing of LIBS or any other analytical techniques for which chemical uniformity over both millimeter and centimeter length scales is required for proper testing. We

[1] M. Verkouteren, G. Gillen, J. Verkouteren, R. Fletcher, E. Windsor and W. Smith, NIST Program to Support T&E of Trace Explosives Detection, ITEA Journal, September/October 2007, 16-18.
[2] E. Windsor, G. Gillen and M. Najarro, NIST Uses Inkjet Printing Technology to Produce Standards for Trace Level Explosive Analysis, www.cstl.nist.gov/projects/fy06/indst0683701.pdf
[3] R. R. Kunz, K. E. Clow, The Trace-Explosives Chemical Background and Its Implication to Trace Detection-Based Counter-IED Operations, MIT Lincoln Laboratory report # 81-1006, 31 January 2007.

achieve these criteria by dissolving the target material in a suitable solvent and spray-coating the solution onto a substrate of choice. Verification of surface loading is achieved by re-dissolving the sprayed analyte and comparing recovered amounts with those found in both calibration solutions and similarly-extracted known controls. This approach to sample preparation is suitable for any soluble EERC sufficiently stable and nonvolatile to not undergo sample evolution over the timescale of the experiment. While the approach is completely general, we provide illustration here with specific reference to TNT deposition only. For demonstrative purposes, we refer to the preparation of a 1" $\times$ 1" aluminum substrate with 0.1 mg/cm^2 TNT, with re-extraction performed using 10 ml of acetonitrile, and with analytical verification performed using a GC-μECD. It should be readily apparent, based on the examples given here, that other desired surface loadings can be prepared by appropriate scaling of solution concentrations and the number of spray doses.

3 Calibration of analytical instrumentation

3.1 *Standard solution preparation:*

In order to verify mass loading of deposited EERCs, it is necessary to first develop a methodology by which the contents of re-dissolved analyte solutions can be compared with known standards. The calibration curves should be made with standards in concentration ranges that are relevant to the study. Guidelines for suitable concentration ranges can be estimated by performing simple mass balances for desired loadings and target areas. With these values as guidelines, standard solutions bracketing this range can be made for calibration purposes.

With reference to the TNT example described above, an order-of-magnitude estimate of the relevant concentrations to be investigated can be made by noting that a total of 0.645 mg TNT are required to obtain a 0.1 mg/cm^2 loading of TNT of the target area. This re-dissolved into 10 ml of acetonitrile with 100% efficiency would yield a 64.5 μg/ml solution, providing an upper bound for the concentration range to be investigated for a target material with this surface loading. In our efforts, aliquots of a 1,000 μg/ml NIST-traceable TNT solutions (e.g. Cerilliant) were diluted in acetonitrile to produce the standards.

3.2 *Analysis of standard solutions:*

With standard solutions prepared, calibration curves used to infer the concentrations of unknown solutions can be generated. The instrument used for all analysis in this effort was an Agilent 6890 GC with a micro-ECD detector. Injection parameters (i.e., 10 μm injection, 5:1 split ratio) and a GC temperature ramp profile (i.e., ramps from 50 ^{o}C to 250 ^{o}C over an 8 min. period) were used. These conditions provided both TNT separation and well-shaped (i.e., Gaussian) retention peaks that were sufficient for the purposes of this work. Calibration curves were generated by testing each known solution (for this example 10, 30, 50, 70, and 90 μg/ml TNT) five times, with solution testing occurring in order of increasing concentration. The integrated TNT peak areas were used to form the basis of a calibration curve allowing peak areas from unknown samples to be correlated with known solution concentration. Figure 1 illustrates a calibration curve generated from a series of suitably-chosen known samples.
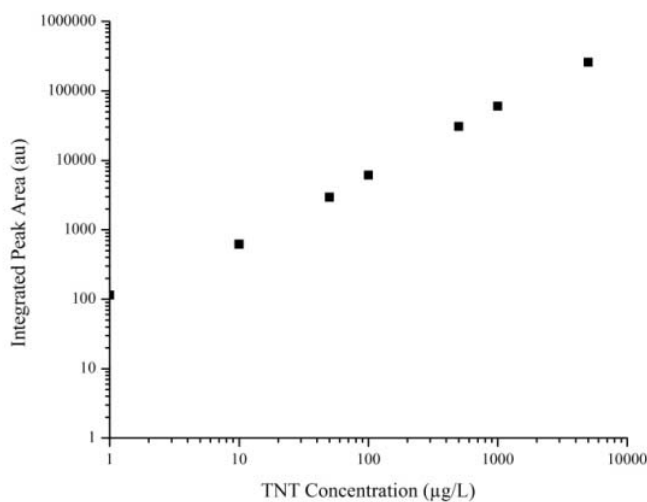
Figure 1: Calibration curve showing integrated GC-µECD peak areas for standard solutions with various TNT concentrations.

4 Calculation of Analyte Extraction Efficiencies from Substrate

In quantifying spray deposition, the amount of material deposited onto a substrate may be inferred by measuring the amount of analyte re-extracted into solution and comparing with amounts obtained for similarly-extracted known samples. In re-extracting, it must be recognized that analytes may not necessarily be recovered from the substrate with 100% efficiency, and that this efficiency might furthermore vary with choice of both analyte and substrate. It is therefore necessary to also quantify the efficiency of the extraction process in order to avoid systematic artifacts generated by sample processing. Towards this end, standard solutions were also drop-deposited onto the aluminum substrates and allowed to dry. Concentrations that would produce target loadings similar to those desired via spray deposition were applied in 100 µl aliquots. This aliquot volume was sufficient to cover the surface – sometimes with the help of additional spreading using a pipette tip – but was not so copious as to cause the liquid front to spill over the side of the substrate wafer.

After solvent evaporation, the deposits were re-extracted and analyzed to account for any systematic discrepancies in recovered mass attributable to the extraction process. It is recognized that while the overall amount of material deposited using both spray and drop deposition would be identical, spatial uniformity and crystal size might differ depending on the method used. In this work it was assumed that re-dissolution was neither a function of the manner in which the material was deposited nor limited by the dissolution kinetics at play under the processing conditions adopted. Variation of extraction times and solvent volumes resulted in similar extraction efficiencies, suggesting that kinetics of dissolution were in fact not critical factors when comparing samples generated by different deposition methods.

With aid of the previously-determined calibration curves, the concentration of the extracted solution, and by extension, the total amount of TNT extracted can be determined. Comparison of the recovered amount

with that originally deposited allows the extraction efficiency to be determined in turn. With both extraction efficiency and calibration curves in hand, the accurate quantification of the amount of material deposited during spraying is made possible.
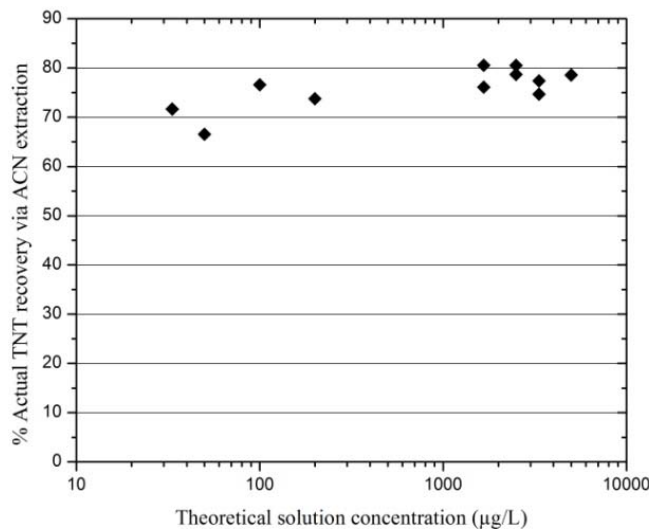
Figure 2: Extraction efficiency determined for extraction volumes resulting in various theoretical solution concentrations. Theoretical concentrations assume 100% extraction efficiency.

Figure 2 shows extraction efficiencies measured for various extracted samples. In this effort, extraction was performed by placing each of the drop-cast substrates face-up into a 100 ml jar (diameter = 2 in) and submersing it in 10 ml HPLC-grade acetonitrile. The jars were agitated on an orbital shaker for 1h and the resulting solutions analyzed. Five replicates of each surface loading were produced and re-extracted for analysis.

5   Target presentation

For reproducible sample dosing, the targets must be mounted in such a way that allows consistent substrate exposure to the spray plume. Presentation of the substrate must take into consideration the facts that i) care must be taken to prevent contamination by residues from previous deposition attempts, and that ii) plume density varies with position. The approach adopted for this effort was to mount the target behind a mask at a fixed position from the spray nozzle. This allowed control of nozzle standoff while allowing only a predetermined area to be exposed to the spray. Figure 3 (left) shows the targets being placed on a stand, while Figure 3 (right) shows the stand with mask being maneuvered into position for deposition.

6   Spray production

When reproducibly spray-dosing homogeneous films, it is important to ensure that time-averaged spatio-temporal inhomogeneities in the plume are much larger than the area to be coated. It is also important to avoid shot-to-shot loading variations. It is therefore necessary to choose a spraying device meeting these

requirements. In dosing a 1"-squared surface, a number of economical sprayers offering the necessary capabilities are readily available. For this effort, a simple Craftsman model #15002 Detail and Touch-up Spray gun was chosen due to its ready availability and low cost. In order to eliminate operator-dependent shot-to-shot variability, the sprayer was fastened to a stand and the trigger depression automated. A servo-activated plunger was developed to fully depress and then release the gun trigger with strokes of consistent force and duration. The servo motion was computer controlled, allowing the number of shots as well as their tempo to be reproducibly administered. The spray gun mounting stand and the target stand can be seen in Figure 4, which also shows a high-speed image of a TNT/acetonitrile solution being sprayed onto the sample substrate. Pure compressed air was used as a propellant to avoid introduction of compressor-related impurities. Visual inspection of the spray plume showed that the automated puffing arrangement minimizes the shot-to-shot variation during consecutive spray dosings.
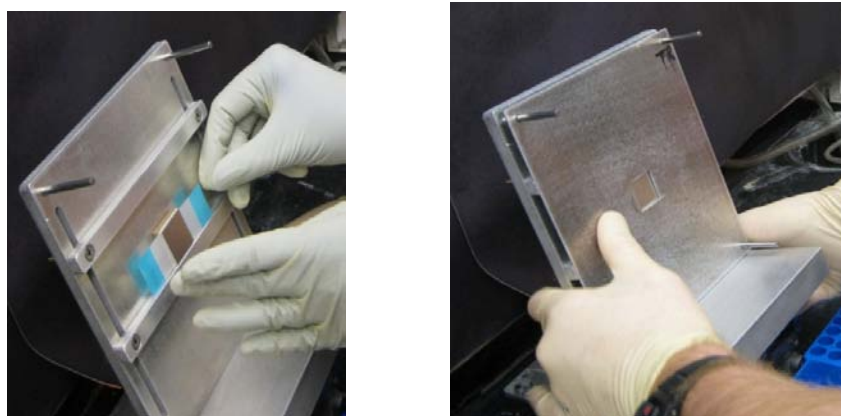
Figure 3: Target stand, unmasked with the target substrate shown (left), and with the deposition mask in place over the substrate (right).
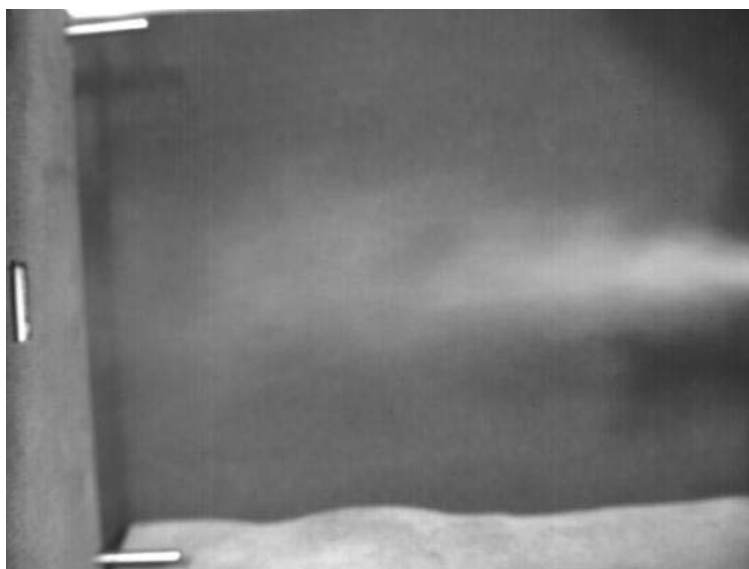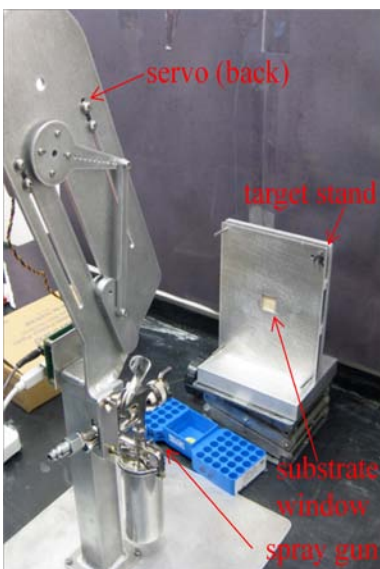
Figure 4: (Left) Spray gun and servo mounted on the spray gun stand, with aligned target stand, mounted substrate and deposition mask also visible. (Right) Imagery of TNT/acetonitrile plume impinging on masked substrate.

7 Preparation of TNT-Coated Sample Substrates

7.1 Spray Gun and Target Alignment:

The spray gun and target stands should be arranged so that the substrate window (figure 3) is aligned in the center of the sprayed mist. The minimum standoff distance should be sufficiently large so as to prevent visible beading or running of drops when a single pulse is sprayed onto a smooth surface. At the same time, it is beneficial for the standoff distance to be sufficiently short so as to limit the amount of material lost to the area surrounding the target. During spraying it is possible for the carrier solvent to undergo significant volatilization as the plume travels along its trajectory, resulting in less analyte being delivered to the target. This can be easily illustrated by visual examination of a spray pattern produced on a smooth surface at various nozzle distances. When acetonitrile is used as a solvent, a dense pattern forms on targets close to the nozzle, while virtually no liquid acetonitrile is deposited at larger distances despite the fact that a vigorous vapor stream clearly impinges upon the target area. In contrast, a healthy dose of liquid water (a solvent with lower vapor pressure) may still be deposited at substantial distances. While viscosity and surface tension effects also play a role in nebulization and plume transport in these examples, it is clear that the effects of rapid droplet evaporation must be considered during setup, particularly for high-vapor-pressure solvents. As a consequence, the amount of solute-carrying solvent actually delivered to the surface is a strong function of distance, with standoff needing to be balanced accordingly.

In our own effort the optimal distance between the tip of the spray gun nozzle and sample substrate was determined to be 15 cm. This configuration resulted in a well-dispersed pattern of acetonitrile droplets with no visibly coalescing liquid, and in a target window subtending ~5% of the solid angle in front of the nozzle. By noting both total spray volume and performing an analysis of the total amount of explosive deposited onto a target, the actual fraction of spray volume landing on the surface could be calculated. In this configuration, the total analyte deposition efficiency per nozzle puff was determined to be 2%.

7.2 Estimation of the required concentration for Spraying TNT:

Given a known efficiency for spray deposition, it is possible to estimate the TNT concentration that should be required to produce a desired surface coverage. Alternatively, a solution concentration needed to produce a target surface loading via a series of pulses may be calculated in favor of one achieving the same end loading with a single spray dose. This multiple-spray approach might be preferable, because it allows for the stepwise addition of material in situations where single-dose depositions might require inconveniently high solution concentrations. An additional advantage of the multiple-deposition approach is that a series of sequential dosings would better mask any random inconsistencies generated during single doses, thereby yielding surface coverages with lower variance between samples. With a known spray volume of P (ml) and a deposition efficiency of X%, 10 sprays of a TNT solution onto a 1 in^2 target resulting in a 0.1mg/cm2 final coverage would require an initial TNT concentration, C_{TNT}, of

$$C_{TNT} = \frac{0.1\frac{mg}{cm^2} \times 6.45 cm^2}{10\ sprays\ \times 0.0X \times \text{P}\ \frac{ml}{spray}}$$

In our own efforts, a sequential deposition of 10 doses was chosen. In our illustration, a spraying efficiency of 2% would necessitate an initial solution concentration of 6.45 mg/ml TNT.

7.3 *Spray Deposition of TNT Solution:*

Applying the concentration estimated in paragraph 7.2, a sample can be prepared by spraying the required doses at suitable intervals. The suitability of the delay between intervals should be determined by duly noting the drying time of a representative spray pattern. In the effort reported here, 12 spray shots were programmed, with a 10s delay between each to allow adequate drying between shots. The two extra spray shots were used at the beginning of the sequence to prime the spray system and ensure that each deposition sequence is performed under identical starting conditions; the plumes of these extra shots being discarded and not otherwise contributing to the deposition process.

With the spray sequence complete, the samples could either be prepared for analysis as described in paragraphs 5 and 6 above, or used as test samples in situations where the resulting surface loading had been verified. In situations where the actual surface coverage differs significantly from that estimated in paragraph 7.2, either the number of spray shots or the solution concentration should be modified accordingly, and the result in turn re-verified. As an example, if a surface mass loading was 25% of that expected, either the TNT concentration for the spray reservoir or the number of spray shots could be increased factor of 4. The appropriate adjustment should intelligently balance the effort required to change the reservoir concentration vis-à-vis the increased time commitment involved in producing an extended series of samples with an extended sequence of deposition shots.

8   Validation of Mass Loading Reproducibility

The reproducibility of the spray-dosing process can be determined by preparing a number of analyte-coated substrates using the fully-optimized deposition conditions described in paragraph 7 and comparing extracted quantities following the analysis outlined in paragraphs 3 and 4. Any sufficiently large variance between samples should be used as an indication that the protocol should be examined to determine the source of the variance. In the effort described in this work, variance between the TNT loadings of a 5-sample sample set was on the order of 3% from specimen to specimen. This repeatability was deemed sufficient for the preparation of sample targets used for LIBS experimentation.

## 9   Verification of Enhanced Spatial Homogeneity

The effect of spray deposition on analyte spatial uniformity can be qualitatively inferred via optical microscopy of variously-prepared surfaces. In order to compare residue distribution from spray dosing with that of drop deposition, TNT/acetonitrile solutions were dosed onto test surfaces via either drop or spray deposition. In notable deviation from the $100\mu g/cm^2$ surface loadings used for illustrative reference in previous sections, the dosings applied via each deposition method were chosen to produce $0.1\mu g/cm^2$ TNT loadings over a 1-in^2 area. This value was chosen because it was recognized that lower loadings could allow easier visualization of residue deposits. In an additional departure from the aluminum targets described earlier, epitaxial-ready silicon wafers were used as substrates so that the residue would be even more plainly viewable. Since wafer features (RMS roughness of <1nm) are orders of magnitude smaller than the dimensions of typical residue particles, use of Si wafers as targets allowed particle distributions

to be clearly resolved without obfuscation by complex topologies typical of more field-relevant substrates. An additional advantage of silicon wafers is the fact that silicon is highly wettable to numerous solvents, which causes large droplets to spread dramatically. Although spreading and wetting dynamics over a Si wafer are certainly different from those observed over aluminum substrates, they are hallmarks of macroscopic wetting phenomena which occur to some extent during all drop-coating process. Recognizing this, the choice of a Si surface serves as a dramatic illustrator of problems characteristic to the drop-coating approach in general.

Drop dosing was conducted by the stepwise addition of four (4) 25-µl aliquots of 6452µg/L TNT in ACN onto an approximately 1x1" area of the Si wafer, with complete drying of ACN before application of any subsequent doses. In contrast with 1x1" Al wafers, where surface and roughness effects easily allow retention of 100 µl of solution without drop spreading, each 25 µl aliquot instantly spread over an area roughly three (3) square inches in size, with no ready means of controlling the direction or extent of spreading at hand. The initial spread of the liquid front was followed by evaporatively-induced flow within the droplet and in a droplet interface which then receded into a few widely-spaced droplets as the remaining solvent dried. Regions of concentrated analyte were visible wherever the last drops of the receding analyte front had come to rest. These regions of dried analyte were in turn re-dissolved by each subsequent application of solvent, which similarly left residues at random positions on the affected surface.

Figures 5 and 6 show optical micrographs of residues produced through drop deposition. It can be seen that particles of various sizes are found within the concentrated residue of each remaining drop, whereas regions outside of the droplet displayed comparatively little material. (While not shown here, it should be noted that untreated wafers showed no appreciable features at magnifications between 5x and 100x.)   The vast preponderance of material applied to the dosed area was clearly concentrated into the residue left by a few drops which were widely separated relative to the dimensions of a typical LIBS beam. This indicates a scenario in which significant nonuniformities in analyte surface loading would clearly cause uncontrollable deviations in shot-to-shot performance should such drop-dosed samples be employed in a LIBS experiment.

In marked contrast, Figure 7 shows dark-field micrographs of TNT from random regions of three different Si wafers prepared in accordance with the procedure described in paragraph 7.3. All three images show TNT particles with dramatically higher dispersion and greater size uniformity than that observed for residues produced via drop-coating. The small size of the aerosol droplets and their dispersion allowed much more even distribution of TNT over areas comparable to LIBS probe beam dimensions. It is clear that shot-to-shot variation in LIBS performed on spray-dosed surfaces should be considerably less dependent on the position of the interrogating beam along the dosed surface. This improved sample quality occurred in spite of the clearly disadvantageous wetting characteristics of the wafer surface to larger drops, and illustrates the advantage gained by delivering the target material via a spraying technique.
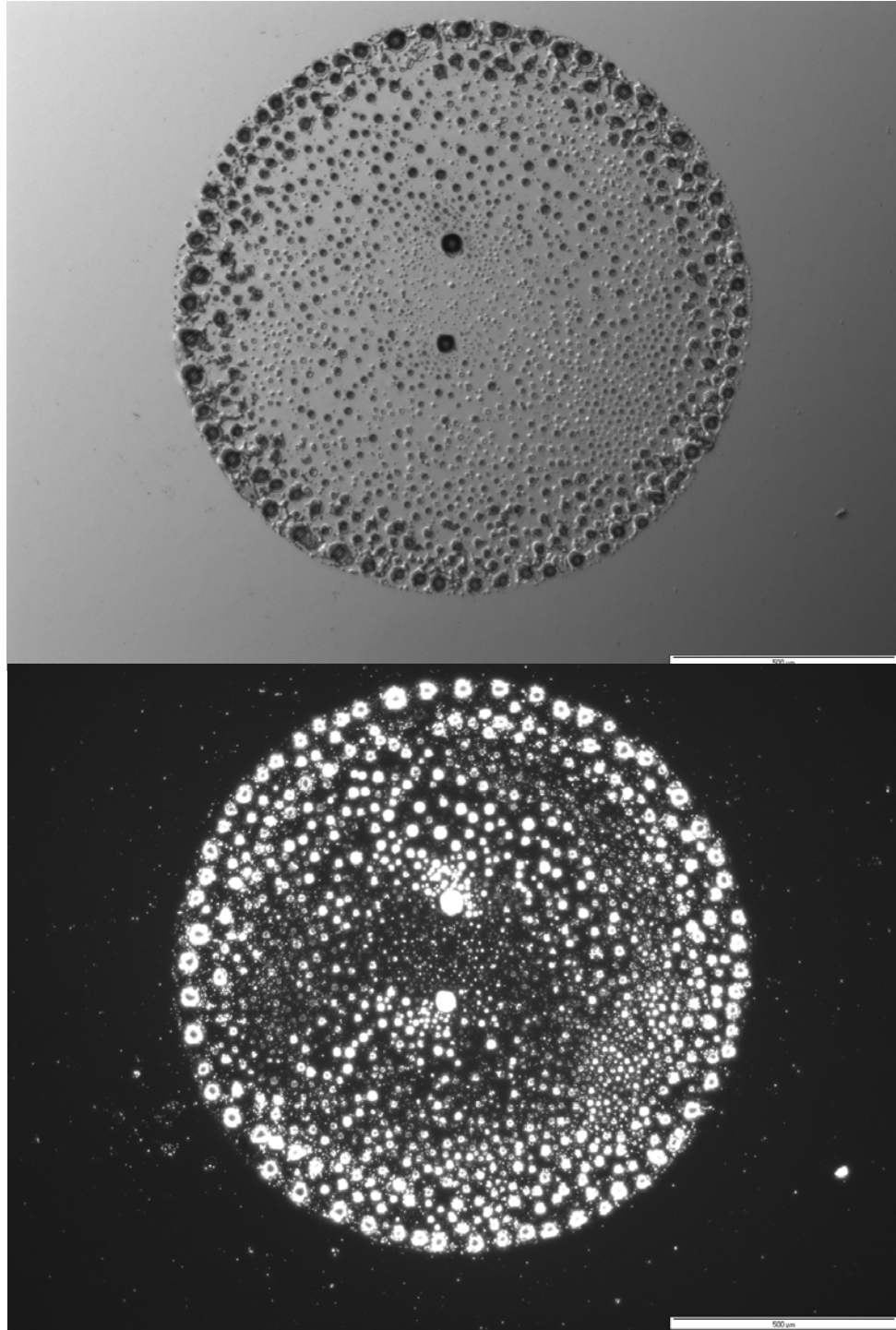
Figure 5: (Top) 5x bright-field micrograph of TNT residue left from drop-deposition of dissolved TNT onto silicon wafers. (Bottom) Dark-field micrograph of the same area. The scale bar for both images spans 500 µm. It is important to note that the spatial loading of TNT shown is not representative of that observed for a majority of the dosed area, which in comparison is essentially devoid of dried deposits.
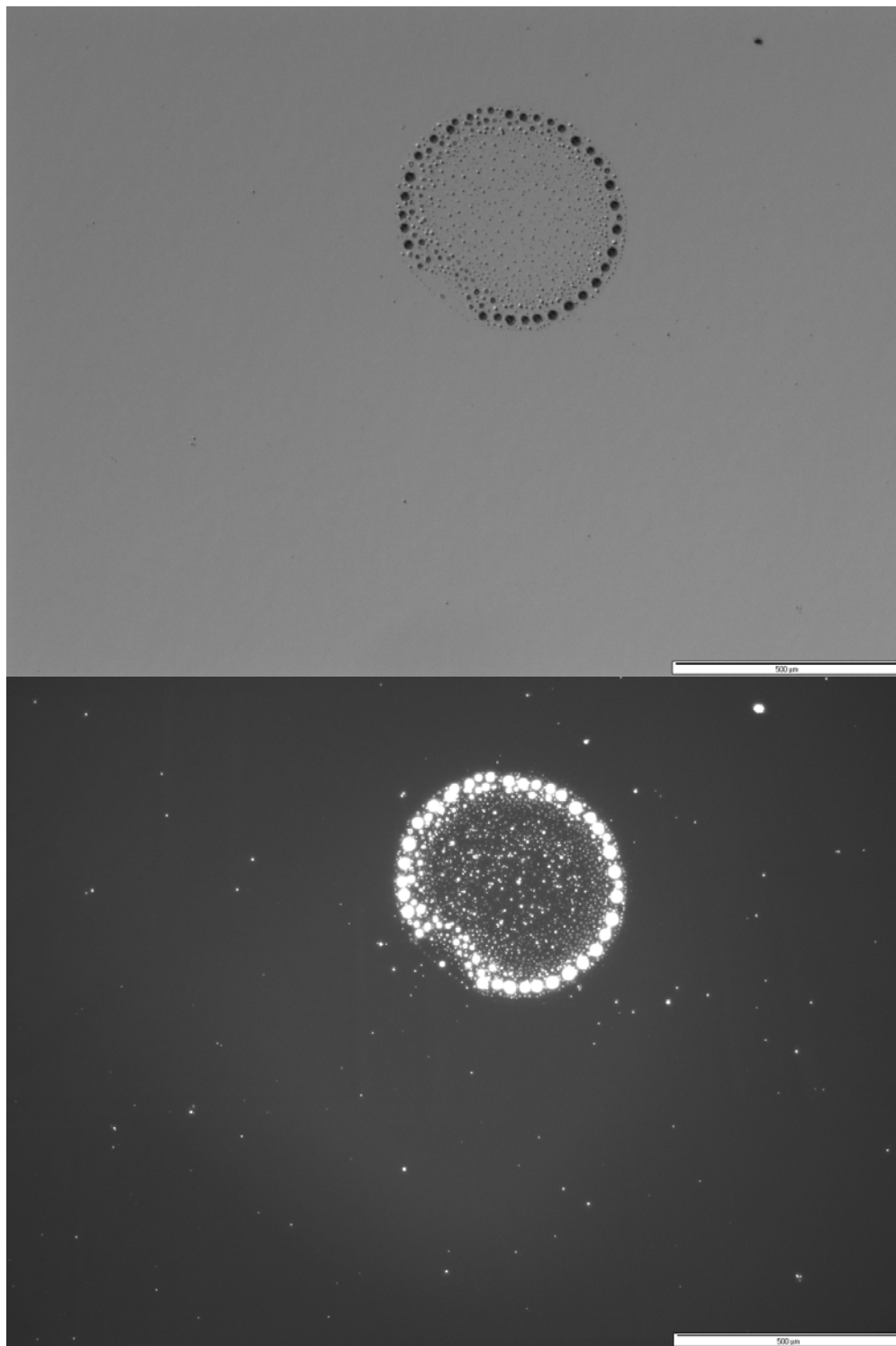
Figure 6: (Top) 5x bright-field micrograph of TNT residue left from drop-deposition of dissolved TNT onto silicon wafers. (Bottom) Dark-field micrograph of the same area. The scale bar for both images spans 500 µm. It is important to note that the spatial loading of TNT shown is not representative of that observed for a majority of the dosed area, which in comparison is essentially devoid of dried deposits.
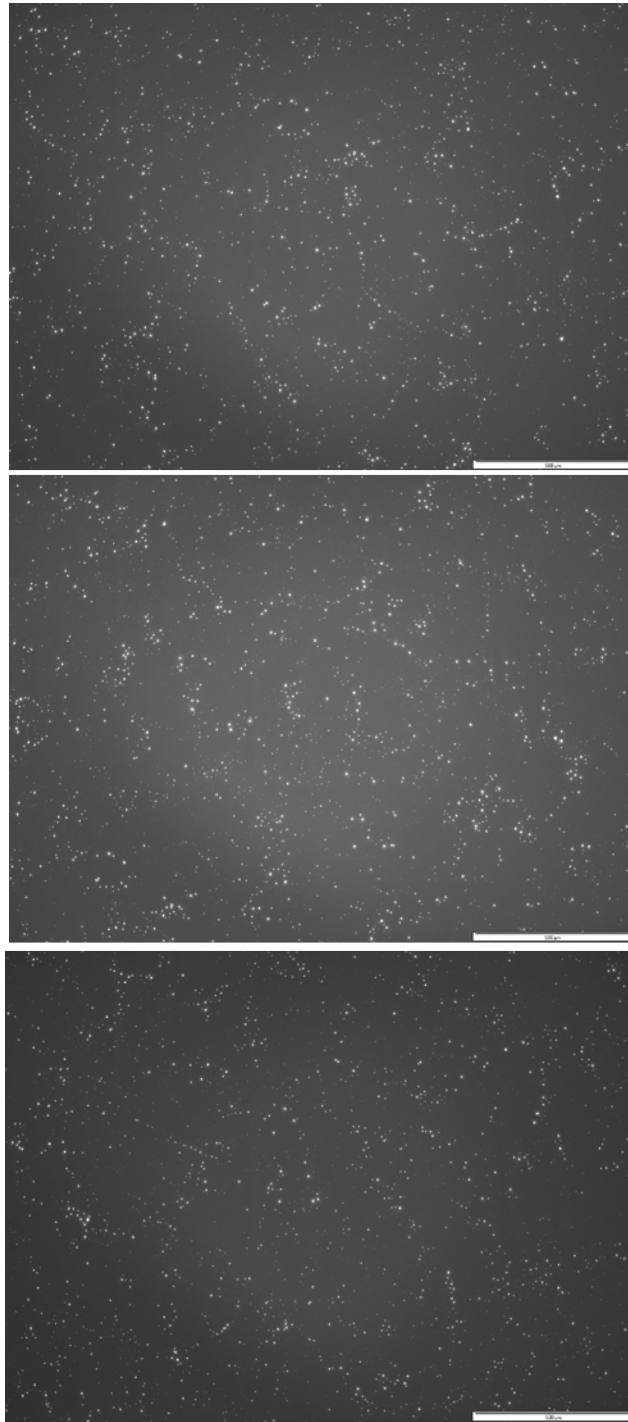
Figure 7: 5x bright-field micrographs of TNT deposited onto silicon wafers by means of spray deposition. Scale bars in all images span 500 µm. Homogeneity in particle distribution is considerably greater than that resulting from drop coating (c.f. figures 5 and 6); in particular over length scales relevant to the diameter of typical LIBS interrogating beams ($\sim$1mm^2).

10 Summary

This document illustrates a method developed by NVESD scientists to rapidly deposit even loadings of trace explosives and related chemicals onto a surface by means of spray deposition. The ability of nebulizing sprays to deliver reproducible mass loadings has been verified with a laboratory GC-µECD running with a profile optimized to resolve TNT residues. Suitable particle dispersion and favorable particle size uniformity have furthermore been corroborated in both high-speed imagery of the spray plume and optical micrographs of the resulting residues. The resulting analyte dispersion and size uniformity were vastly superior to those of samples prepared via drop dosing, even when an otherwise highly-wettable surface was sprayed. The examples presented here are quite general, and approach may clearly be extended to other substrates and other soluble EERCs.

While the technique poses many attractive advantages for test sample generation, it must be considered only one possible approach to sample dosing. For the sensor developer evaluating the suitability of spraying to sample preparation, it should be noted that a significant fraction of the spray plume may be expected to not land on the target area. Any attempt to achieve a loading of 0.1 mg/cm^2 using this approach will necessarily result in the loss of notable amounts of analyte and solvent to both the atmosphere and the immediate vicinity of the target. As a consequence, the utility of this approach – namely its technical simplicity and ease of implementation – must be duly weighed with the economics of the consumable materials involved.

Distribution for Report: RDER-NV-TR-265

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