Ink Jet Metrology: New Developments at NIST to Produce Test Materials for Security Applications

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Abstract

Reliable measurements and deposition control are critical to the success of ink jet applications. We report gravimetric and optical measurements of microdroplets that enable high-accuracy drop-on-demand (DOD) ink jet printing, which has been applied to the production of materials for testing trace and stand-off explosives detectors deployed at airports and other locations. The imprecision of solute mass deposition is typically less than 0.4 % while the combined standard uncertainty is less than 1 %. Applications include the production of trace explosives reference swipes, the manufacture of standard microspheres by drying droplets either in flight or on superhydrophobic surfaces, and the generation of trace explosives vapors. The gravimetric measurement capabilities of the system have also enabled testing and calibration of grayscale thresholding routines used in optical micro-dimensional analysis of droplets in flight.

INTRODUCTION

Trace detection is a primary strategy for thwarting terrorism in the US and abroad. We are working with the U.S. Department of Homeland Security (DHS) Science and Technology Directorate, the DHS Transportation Security Laboratory, and the NIST Office of Law Enforcement Standards to strengthen the metrology system that supports the widespread operational deployment of explosive trace detectors (ETDs). A major aspect is the development of realistically designed test materials for assuring the reliability of trace detection, and we have adapted ink jet technologies for the purpose. Ink jet metrology, i.e. the infrastructure of facilities, materials and methods needed for accurately measuring droplet characteristics during non-contact printing, is being established at NIST [1-3]. This is enabling a multitude of applications related to homeland security, including the production of swipe materials for testing the performance of ETDs, the generation of trace vapors for calibrating explosive vapor detectors, and the production of standard particles and thin films useful for testing sampling strategies and stand-off detection. Another outcome has been the ability to accurately calibrate optical systems using gravimetric measurements. The gravimetric and optical methods developed for ink jet deposition are briefly described, as well as several homeland security applications that have been developed by the various authors.

EXPERIMENTAL

Our drop-on-demand ink jet printing systems are manufactured by MicroFab Technologies,* to which we often interface various controls and sensors in order to monitor, improve and extend performance. Headspace pressure in the fluid reservoir is controlled through a pressure/vacuum regulator (MKS PC90) using feedback from a differential pressure transducer (MKS 698A) referencing the headspace to ambient barometric pressure. Average droplet mass is determined by ejecting a known number of droplets (typically 20 000) into a capsule positioned on a submicrogram balance and correcting for evaporation and other effects [1]. Droplet imaging is performed using the JetXpert system manufactured by ImageXpert, where images of individual droplets within an ejection sequence may be captured to monitor droplet formation processes and delineate non-periodic events. Solute concentrations are validated through a variety of analytical techniques, including GC-MS, HPLC, and UV-vis. Evaluation of uncertainty indicates that the combined standard uncertainty for delivering solutes in fluids through our ink jet systems is less than 1 %, while the imprecision in repeated determinations is less than 0.4 % (Figure 1). The driving waveform, the ejection cycle period, the fluidic pressure, and the sequence position of a droplet in a burst all influence the dispensed mass by a host of mechanisms, including acoustic resonance interactions, orifice refill dynamics, and first-drop and last-drop effects [3].

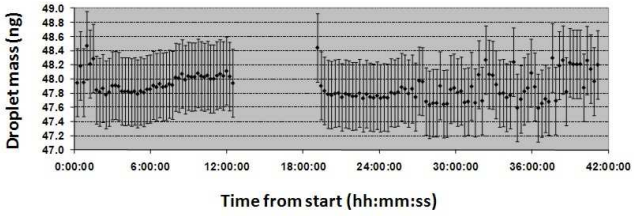

Figure 1. *Repeatability of ink jet deposition as measured by gravimetry across 42 h. Measurements were repeated every 16 m except during a scheduled break of about 6 h. Error bars are estimated combined standard uncertainties of individual measurements.*

* Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

APPLICATIONS

Test Materials for ETDs and Forensics

NIST uses a MicroFab Jetlab4 XL-4 printer system having an integrated submicrogram balance and precision motion stages. The x-y stage holds a variety of templates on which we may position sampling substrates and other objects for inkjet deposition of trace explosives and associated compounds (Figure 2). A selected number of droplets from a standardized solution, which contain the desired trace amount of solute, are precisely deposited on the surface of each substrate. The small volume of dispensed fluid enabled by ink jet deposition allows fast evaporation before the fluid wicks into the substrate, leaving most of the solute on the upper surfaces. This is important for realism since, at security checkpoints, swiping also results in residues atop the surface of the sampling substrate. The substrate is placed into a thermal desorber that heats the sample, releasing vapors for detection if explosives are present.

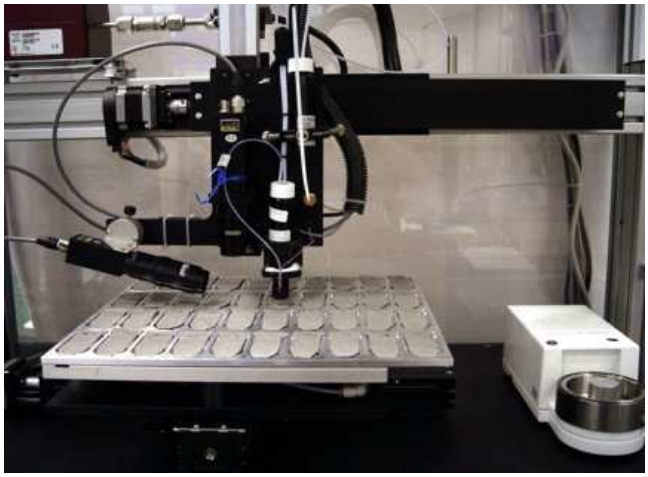

Figure 2. *Precision printing of explosive compounds on substrates for the testing of trace detectors.*

We have been successful at preparing trace explosive test materials at dosages spanning many orders of magnitude simply by changing the number of droplets deposited from a standard solution. For large numbers of droplets, these may be precisely applied in arrays within the small area of the substrate that is heated by the thermal desorber. Substrates containing explosives such as cyclotrimethylenetrinitramine (RDX), 2,4,6-trinitro-toluene (TNT) and pentaerythritol tetranitrate (PETN) have been prepared by this method. The printing of simulated fingerprints has also been demonstrated, which provides a means to fabricate a standard residue for forensic training purposes.

Designed residues, which may be comprised of an array of particle microspheres at one extreme, to a uniform layer of compound at the other extreme, may be prepared by controlling the spatial deposition of the fluid and the contact angle of the fluid on the applied surface. In one such example, aqueous solutions of ammonium nitrate were deposited onto a superhydrophobic surface prepared at the NIST Center for Nanoscale Science and Technology by an all-plasma surface

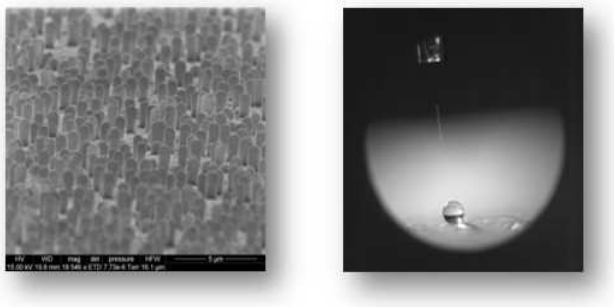

Figure 3. *(Left) Environmental scanning electron micrographs (ESEM) of superhydrophobic surface, showing nano-pillars of fluorinated polymer. (Right) Optical micrograph of aqueous sphere being grown by DOD ink jet deposition on superhydrophobic surface.*

modification process (Figure 3) [4]. The surface consisted of nano-pillars of fluorinated polymer that provided contact angles greater than 150° with water. An array of solid microspheres was made by depositing bursts of aqueous microdrops on this surface and allowing the water to evaporate from the spherical drop, which shrank and quickly transitioned to solid ammonium nitrate. In another example, a self-assembled monolayer (SAM) of chloro-dimethyl-n-octylsilane was formed on silicon wafers by vapor deposition [5], yielding a hydrophobic surface with a water contact angle of approximately 90°. The contact angle may be further tailored by timed exposure to UV light to generate surfaces with water contact angles varying from ≈ 90° to < 10°.

Standard Particle Production

Specialized particles are produced by ink jet deposition in tailored environments. These materials are used to test and optimize manual, automated and aerodynamic particle sampling methods used in explosive screening. Standard particles are produced by ejecting droplets through a vertical drying tube and evaporating the droplets in flight, leaving behind solute particles. Particle sizes are predicated by tailoring the ejected droplet size as well as by coalescence of a known number of droplets in bursts, where the slower first drop in a burst acts as the nucleating entity. RDX and ammonium nitrate particles prepared in this manner are shown in Figure 4.

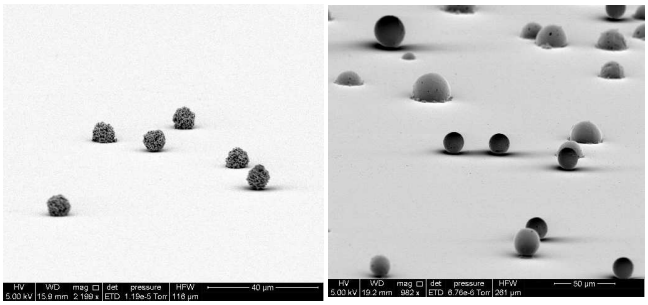

Figure 4. *ESEM of RDX particles (left) and ammonium nitrate particles (right). Each RDX particle (8 µm diameter) was made by coalescence of a 5 droplet burst of isopropanol solution. Because of challenges in ejecting aqueous solutions, the diameters of the ammonium nitrate particles ranged from 14 µm to 28 µm; the larger particles were not completely dry when impacting the silicon surface.*

Trace Vapor Generation

The NIST ink jet vapor generator ejects fluid droplets containing trace explosives onto a heated surface (Figure 5). The resulting vapor plume is diluted into a calibrated air stream, where explosive vapor signatures may be produced at fg/L to ng/L levels. Using this generator, explosive vapor sniffers may be calibrated

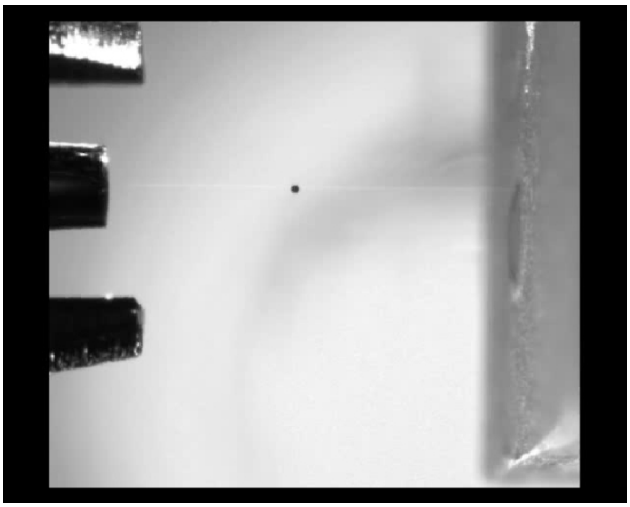

Figure 5. *Ink jet droplets containing a trace explosive are ejected horizontally onto a surface heated to a temperature in the sub-boiling regime of the fluid. When conditions are right, the composition of vapor evaporating from the stable pool of fluid on the surface is the same as the composition of the impinging droplets.*

and next-generation detectors may be tested and validated. The design of the system takes into account the upward direction of the thermal vapor plume in order to minimize wall effects; i.e., interactions of the explosive vapor with cooler surfaces such as glass walls and the ink jet nozzle (Figure 6). Photoionization measurements of the emerging fluid vapor show that the residence time for vapors within the generator is typically less than 10 s, and that the variation in output across one hour is below the imprecision (1.7 %) of the measurement.

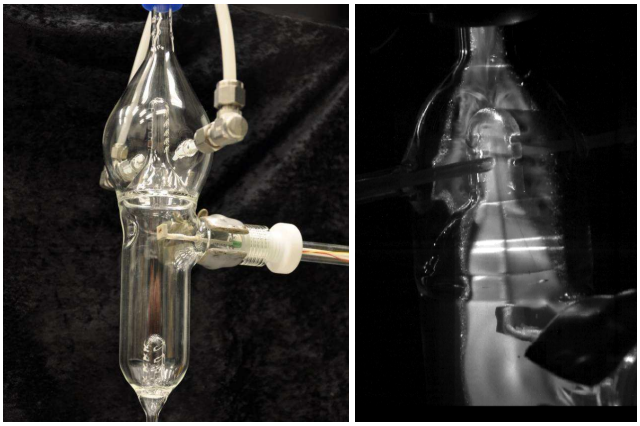

Figure 6. *The NIST ink jet trace vapor generator (left image) and close-up view of top portion (right image, containing theatrical fog for flow visualization).*

An advantage of DOD ink jet vapor generation is the programmability of the desired vapor signature, which may be delivered continuously or in pulses, and at levels that span over seven orders of magnitude. Figure 7 shows the response of a FIDO XT trace vapor sniffer to a pulse of TNT generated every 90 seconds. The amount of TNT in each pulse was programmed to increase slightly to compensate for the expected loss in sensitivity of the detector during the test. The compensated variability of the detector could therefore be measured directly.

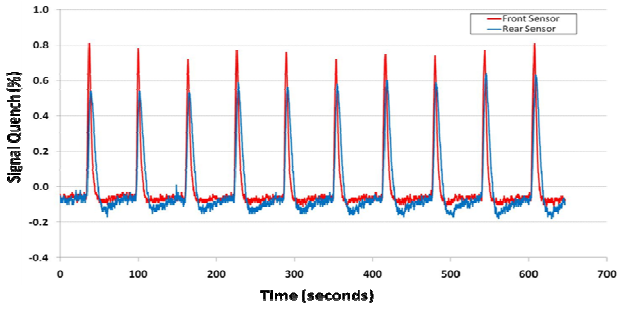

Figure 7. *Response of an explosive sniffer to programmed pulses of trace TNT vapors generated by the NIST ink jet system.*

Metrology and Gravimetric Calibration of Optical Thresholds

Our gravimetric method offers an approach to microdrop sizing that has the benefit of high precision and strong traceability to the Systeme Internationale (SI). Using the density of the fluid, the measured mass of a spherical droplet may be converted to diameter. The uncertainty of such an approach, which is dependent on the combined uncertainties in the gravimetric measurement, the fluid density and the aspect ratio of the droplet, can amount to less than 1 %. Mass determination based on optical measurements of droplet diameter is inherently prone to

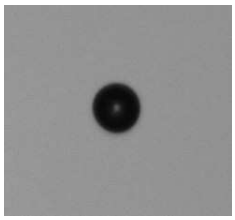

Figure 8. *Focused droplet image. The bright spot in the center is the defocused image of the illuminator, which is focused in front of the droplet.*

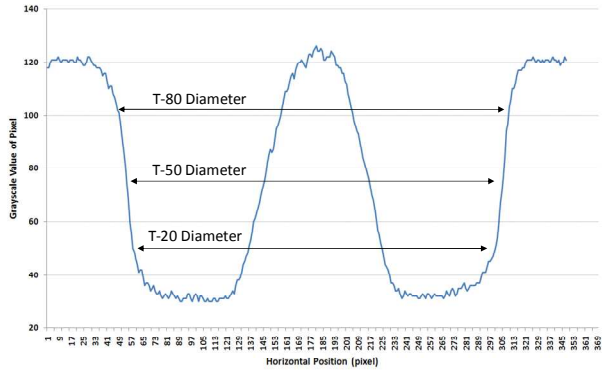

Figure 9. *Grayscale profile across center of droplet image. The diameter measurement depends on the adopted grayscale threshold, and varies by 8 % between the T-20 and T-80 diameters, which are defined by the grayscale values at 20 % and 80 % of the grayscale range.*

high uncertainties because the volume increases as the cube of the radius. For example, if a diameter measurement is inaccurate by 5 % (such as 105 µm instead of 100 µm), the volume (and thus mass) calculated from that diameter will be inaccurate by 15 % (in our example, 0.602 µL instead of 0.524 µL). Optical methods depend on accurate delineation of droplet boundaries, the uncertainties of which are due to many factors, including refraction, lensing effects, and physical differences between calibration artifacts and the microdrops in flight (Figures 8 and 9). Numerous efforts have been performed in understanding and correcting for these factors in order to better characterize the sizes and shapes of microdrops by optical means, yet many uncertainties remain. Imaging programs frequently give the user many thresholding options based on various optical and statistical assumptions, with each method prone to particular biases and the set of methods offering a range of results. Using gravimetrically-determined droplet dimensions, we have found that the Otsu method [6] for delineating droplet boundaries works well under controlled conditions.

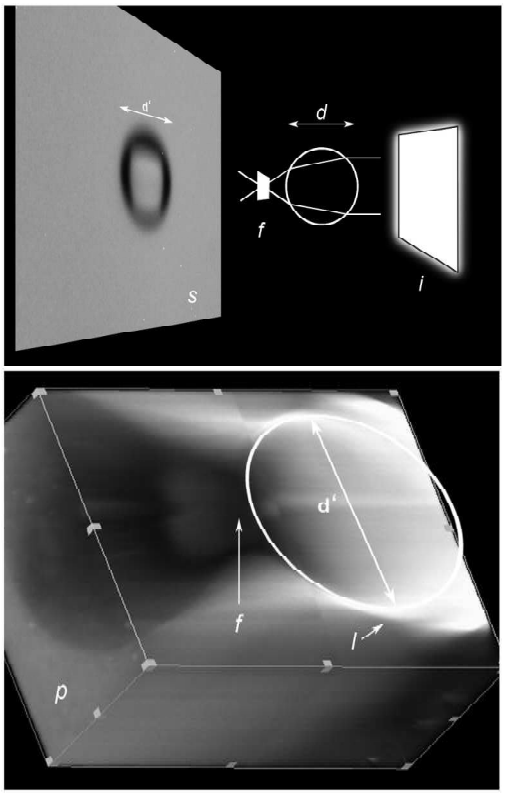

Figure 10. *Top: schematic showing spherical droplet of true diameter (d), an illuminator (i), the image of the illuminator at the focal point of the sphere (f) and the resulting ink jet system image (s) from which a measured diameter (d') is obtained. Bottom: 3-dimensional empirical investigation of optical paths and effects around the perimeter of a sphere of known diameter (d) with diffraction effects (l) impacting measured diameter (d') and showing focal point (f) and appearance of sphere at a specific plane of focus (p). The 3D reconstruction was performed using Image-Pro Plus 6.2 running 3D Constructor 5.1 (Media Cybernetics, Inc., Bethesda, MD).*

It is useful to explore the limitations of optical measurements from ink jet imaging systems. In progress is a comparison of theoretical focus positions and uncertainties relative to actual optical measurements of light paths and spheres using independently measured diameters (Figure 10). A variety of optical effects are involved that can lead to variations in measurements. These effects include the appearance of light and dark alternating diffraction/refraction lines around the perimeter of the sphere, the extended range of focus, digital pixelation, the different focal planes of the illuminator and the perimeter of the sphere, and uneven illumination. The uncertainties introduced by these factors are being modeled and empirically explored by comparing optical images of spheres of known diameter (Fig. 10 top) to analyze the 3-dimensional optical reconstruction of the effects (Fig. 10 bottom).

References

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Author Biography

Michael Verkouteren received his B.S. degree from Tufts University and Ph.D. from Purdue University (1984). Since then, he has worked in the Surface and Microanalysis Science Division of NIST, focusing on research and standards development projects of importance to US industry, the environment, and homeland security. For the past eight years his work has focused on the trace analysis of explosives, where he has adapted ink jet technology to help develop standards, test materials and metrics for measuring detector performance. He is a member of the American Chemical Society and ASTM Committee E54 on Homeland Security Applications.