

# 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 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-triazacyclohexane) 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-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 at screening locations including airports, seaports, U.S. embassies, and other government facilities. Although analytical techniques exist to detect quantities of explosives at or below the nanogram (ng) level, most methods cannot handle the high-throughput sampling demands that exist at screening locations.<sup>1–3</sup> Ion mobility spectrometry (IMS) is an analytical technique capable of rapid ( $\approx 10$  s) trace level explosive analysis. Commercially available IMS systems are rugged, portable, and capable of operating at atmospheric pressure. For these reasons, IMS instruments have been widely deployed. It is estimated that approximately ten thousand IMS instruments are in use for trace-level explosive screening.<sup>4</sup> For this work, we define trace detection as chemical analysis of explosive residues at masses between 0.1 and 100 ng.

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 surfaces and collected onto the traps. Traps are then introduced into the IMS instrument where the explosive particles are vaporized at temperatures exceeding 200 °C. The explosive vapor is then introduced into the ion source region where it is ionized via adduct formation with  $\text{Cl}^-$  reactant ions created by electron impact of a chlorinated reactant gas such as hexachloroethane with a  $\beta$  particle emission from a  $^{63}\text{Ni}$  source. After ionization, the adduct ions are injected into a drift tube where their atmospheric gas phase mobility is determined by their time-of-flight in a weak electric field. Ions travel through the drift tube at different rates depending on their size, shape, and charge, and the measured drift time is compared to a reference library of known explosives for identification.

Test materials (traps) containing known and reproducible (typically nanogram) quantities of explosives are critical for calibrating IMS instruments and ensuring that they are operating properly at deployment locations. Desired properties for such test materials include the following: high precision and accuracy, a large dynamic range in concentration, and scalability to allow high throughput for rapid and inexpensive production to accommodate the large numbers of deployed IMS systems. A variety of different explosive test materials are needed to provide flexibility to respond to the large and often changing number of threats. Using inkjet printing technology to produce trace explosive test materials represents one promising approach to meeting all of these requirements.

Piezoelectric drop-on-demand inkjet printing is a versatile method for the quantitative delivery of microvolumes of solutions.<sup>5</sup> Inkjet printing offers noncontact, high-throughput deposition of precise quantities of materials. The reproducibility of optimized inkjet printers has been reported to be better than 2% relative standard deviation for day-to-day measurements of dispensed volumes.<sup>6</sup> Large dynamic ranges in deposited analyte concentration ( $10^5$ ) are achieved simply by varying the number of drops printed. Over the past decade, inkjet printing technology has

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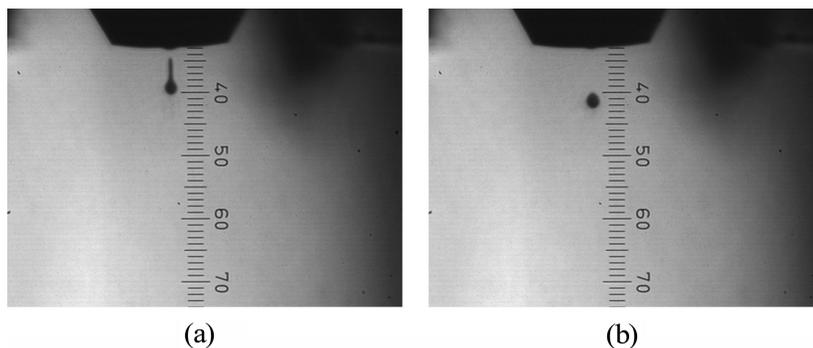
<sup>†</sup> National Institute of Standards and Technology.

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**Figure 1.** Drop generation from Jetlab II piezoelectric ink jet printer. Drops are shown at (a) 100  $\mu\text{s}$  after drop generation and (b) 150  $\mu\text{s}$  after drop generation. Each division on scale = 32  $\mu\text{m}$ .

been widely applied to diverse applications ranging from the printing of DNA microarrays to dispensing metallic solder for interconnects in the electronics industry.<sup>5,7,8</sup> If explosives can be printed in a reproducible manner, then test materials can be produced rapidly and inexpensively. This paper demonstrates the feasibility of the use of drop-on-demand inkjet printing technology to produce RDX (1,3,5-trinitro-1,3,5 triazacyclohexane) test materials for trace level explosive analysis.

## EXPERIMENTAL SECTION

**Stock RDX Solution.** The high explosive RDX was purchased as standard solutions consisting of individually packaged ampoules (approximately 1 mL) containing the explosive dissolved in either acetonitrile or methyl alcohol at nominal concentrations of 1000  $\mu\text{g}/\text{mL}$  (Restek, Bellefonte, PA; Supelco, Bellefonte, PA; and Cerilliant, Round Rock, TX). (Certain commercial equipment, instruments, or materials are identified in this report 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.) Isotopically labeled RDX ( $^{13}\text{C}_3\text{-}^{15}\text{N}_3\text{-RDX}$ , 99%, Cambridge Isotope Laboratories, Andover MA) at a nominal concentration of 1000  $\mu\text{g}/\text{mL}$  was obtained for use as an internal standard for gas chromatography/mass spectrometry (GC/MS) quantitative analysis.

We have found that typical solvents used to dissolve explosives are not optimal for printing. The rheological properties of solvents such as acetonitrile, methanol, and tetrahydrofuran are outside the typical range needed for stable operation of our printer systems (kinematic viscosity  $1 \times 10^{-6}$ – $30 \times 10^{-6}$   $\text{m}^2/\text{s}$  and surface tension 0.02–0.06  $\text{N}/\text{m}$ ).<sup>5</sup> To achieve printer stability, explosives were reconstituted in isobutyl alcohol (IBA). Reconstitution was achieved by transferring a known volume of explosive solution to a 30 mL inkjet printer bottle, allowing the solvent to evaporate, and then redissolving the remaining explosive residue in IBA. Solubility of explosives in IBA is less than the solubility in the original solvents. Therefore, the maximum explosive concentrations of the reconstituted inkjet printer solutions are often <200  $\mu\text{g}/\text{mL}$ . All inkjet printer

solutions are filtered prior to use using 0.2  $\mu\text{m}$  PTFE syringe filters to minimize the possibility of clogging the inkjet printer system.

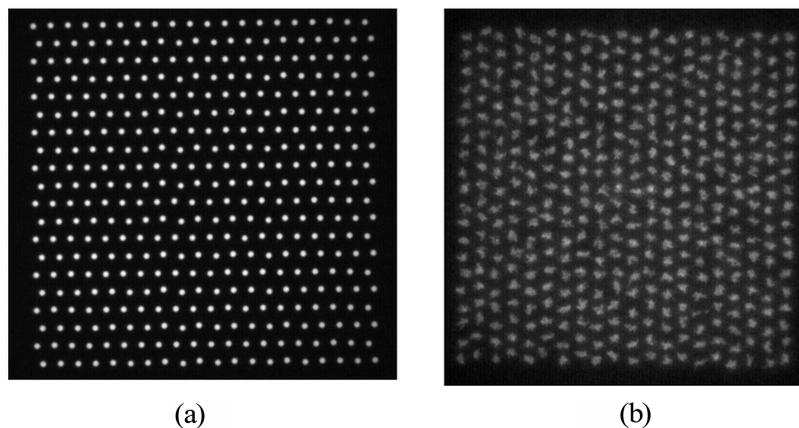
**Inkjet Printing.** Test materials were produced using a Jetlab II (MicroFab, Plano, TX) inkjet printer system. The Jetlab II is a drop-on-demand inkjet printing system with precision X, Y, Z motion control, drop ejection drive electronics, pressure control, and a drop visualization system. The print head consists of a glass capillary tube with a 50  $\mu\text{m}$  diameter orifice surrounded by a piezoelectric crystal. Voltage pulses ( $\approx 20$ –60 V; rise time = 3–5  $\mu\text{s}$ ; dwell time = 20–40  $\mu\text{s}$ ; fall time = 3–5  $\mu\text{s}$ ) applied to the piezo crystal cause it to expand and then contract around the capillary producing an acoustic wave that propagates through the printing fluid in the capillary tube. When an acoustic wave of sufficient energy reaches the orifice, a microdroplet is ejected. Stroboscopic illumination and a charged coupled device (CCD) camera are used to visualize droplet ejection (Figure 1). For stable droplet ejection, the printer conditions are tuned by visually observing the ejected microdrops while adjusting the voltage pulse parameters and the backfill pressure on the fluid in the capillary. Optimal jetting is generally found using conditions that give the highest microdrop velocity without satellite droplet formation. Printing was performed at a frequency of 2000 Hz with a droplet ejection velocity of  $\approx 2$  m/s and an average drop volume of 116 pL (diameter = 60.5  $\mu\text{m}$ ). Detailed studies recently conducted in our laboratory have used advanced gravimetric approaches to rigorously evaluate the effect of voltage pulse parameters, backfill pressure, and drop ejection velocity on printer stability, reproducibility, and droplet size with the goal of developing optimal conditions for future printing studies.<sup>9</sup>

When printing, multiple traps are held in a custom designed sample holder. The print head remains fixed while the precision stage moves from trap-to-trap. We print array patterns containing small numbers of drops (1–10) at each array element rather than a single deposit at one point. This assures rapid evaporation times, minimal bleed-through of solution to the backside of the trap, and presents a more uniform sample to the desorber system of the IMS. Sample throughput is limited by the time required to reposition the stage at each trap. Arrays can be printed using three different methods: drop-on-demand, print on the fly, and print on the fly burst mode. In drop-on-demand mode, the stage moves in discrete increments from array point to array point dispensing one or more drops at each point. With print on the fly, a single

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**Figure 2.** (a) Fluorescence micrograph of an array pattern of single drops ( $20 \times 20$ , 0.3 mm spacing between points) printed on a mixed cellulose ester membrane filter (0.05  $\mu\text{m}$  pore size). (b) Same array printed on quantitative grade ashless filter paper. Fluorescein dye was added to the printer solution to allow drop visibility.

drop is dispensed at each array element while the stage is continuously moving. In print on the fly burst mode, the stage moves continuously but multiple drops are dispensed at each array point. Print on the fly burst mode significantly improves sample throughput. Using the drop-on-demand mode and dispensing one drop at each array element, it took 90 min. With print on the fly mode, dispensing one drop at each array element, this time was reduced to 2 min 48 s, and when print on the fly burst mode is used, dispensing five drops per burst, it took only 24 s. One potential drawback of printing in burst mode is a slight loss of positional accuracy due to spreading or elongation of array point elements. If positional accuracy is critical, then printing should be performed using the single drop mode rather than burst mode. For the present application, this is not thought to be of significant concern.

**Substrate (Trap) Materials.** Visualization of inkjet printed drop patterns on traps is a valuable tool especially during the development of new explosive “ink” solutions. Visualizing printed array patterns is a useful technique for determining whether the printer is performing stably and reproducibly. Drop pattern visibility is achieved by adding fluorescent dye to the printer solution and using substrates that allow visibility such as inkjet paper and membrane filter materials composed of cellulose esters or polycarbonate (Figure 2a).

Although these substrates are useful for inkjet purposes, they cannot be used for the production of trace explosive test materials because they are not thermally stable at the elevated temperatures used during IMS analysis. Therefore, to produce explosive test materials for IMS, it is necessary to print onto thermally stable traps with no volatile compounds that interfere with the IMS analysis. Traps produced by IMS manufacturers (commercially called swipes, filters, or swabs) fulfill these requirements and make good substrates for trace level explosive test materials. The only disadvantage of the manufacturers traps is that inkjet printed patterns are difficult to see due to a high fluorescent background in these materials.

Through trial and error testing, it was determined that ashless grade filter papers (Whatman 41, Middlesex, UK) were compatible with IMS testing temperatures while also allowing adequate visualization of inkjet printed patterns (Figure 2b). A blank IMS analysis performed on the filter paper was observed to deplete

dopant ions in IMS instruments more rapidly than blank analyses performed on manufacturer’s traps. This was most likely due to volatile components on the filter paper. Pretreatment of the filter paper using a solvent wash (acetone soak overnight  $\approx 15$  h) and a thermal treatment (oven at 115  $^{\circ}\text{C}$  overnight) was observed to minimize IMS interference. Therefore, we routinely perform the pretreatments prior to making explosive test materials. Treated filter papers were used for all analyses in this study. The addition of dye to the inkjet printer solution was used during method development and for trouble shooting purposes. To minimize any potential interference with the chemical analysis of the explosives, dye was not used during the production of the actual test materials. An example of a typical inkjet printed pattern is shown in Figure 2. The printer solution was isobutyl alcohol with 25  $\mu\text{g}/\text{mL}$  fluorescein dye added for pattern visibility. An array pattern containing 400 drops ( $20 \times 20$  spots containing 1 drop each) was printed with a drop spacing of 0.3 mm. In Figure 2a, the pattern was printed onto a mixed cellulose ester membrane filter [(0.05  $\mu\text{m}$  pore size), Millipore, Bedford, MA]. Figure 2b shows the same pattern printed onto the ashless grade filter paper.

**Gravimetry.** Mass measurements were made using a Mettler AE 240 analytical balance, a Mettler AT21 Comparator microbalance (Toledo, OH), and a Sartorius SE2-F ultra microbalance (Goettingen, Germany). The repeatability of each balance was determined by making repeated mass measurements of the containers used in this study. Balance accuracy was determined by measuring the mass of calibration weights that were of similar mass to the containers weighed in this study.

**Gas Chromatography/Mass Spectrometry.** Gas chromatography/mass spectrometry analyses were performed using a 1200 Varian (Palo Alto, CA.) GC/MS. Aliquots of 1  $\mu\text{L}$  were isothermally injected (by autosampler) at 150  $^{\circ}\text{C}$  using a split valve injector with a split ratio of 50/1. The GC column (12 m  $\times$  0.22 mm HT-5–SGE, Austin, TX) was operated at a constant helium carrier flow of 6 mL/min and held at 130  $^{\circ}\text{C}$  for 2 min, followed by a 20  $^{\circ}\text{C}/\text{min}$  increase to 160  $^{\circ}\text{C}$  with a 1 min hold. The mass spectrometer was operated in the negative ion chemical ionization (NCI) mode with methane as the reagent gas. For RDX quantitative analysis, an isotopically labeled RDX ( $^{13}\text{C}_3\text{-}^{15}\text{N}_3\text{-RDX}$ , 99%) solution was added as an internal standard (Cambridge Isotope Laboratories, Andover, MA). Ions were monitored at mass/

charge ( $m/z$ ) of 102 and 129 for RDX and at  $m/z$  of 104 and 135 for isotopically labeled RDX at a fixed electron multiplier voltage of 1200 V. The 129  $m/z$  (RDX) and 135  $m/z$  ( $^{13}\text{C}_3\text{-}^{15}\text{N}_3\text{-RDX}$ ) fragment ions were selected for quantitative analysis based on their greater relative abundance. For quantitative purposes, a calibration curve was produced from five standard solutions ranging in RDX concentration from 0.1 to 100  $\mu\text{g}/\text{mL}$ . Each standard solution was prepared by mixing a known mass of RDX standard solution with a known quantity of the isotopically labeled RDX internal standard. These calibration solutions were used to determine instrument response factors that were then used to quantify the amount of RDX dispensed from the inkjet printer.

Inkjet-produced samples were prepared for GC/MS analysis by inkjet printing into deactivated glass inserts placed within GC/MS sample vials. When printing into inserts, fluid was sometimes observed on the sides of the inserts indicating that the droplet trajectory was not always straight down into the bottom of the insert. To ensure that no explosive was lost prior to GC/MS analysis, the inkjet nozzle was inserted approximately halfway into the insert, the drops were dispensed, and then the nozzle was removed. The internal standard was added by pipet, and the inserts were filled with solvent to a final volume of 250  $\mu\text{L}$ . Adding additional solvent to recover explosive from the sides of the inserts required that a larger number of drops be printed to achieve the desired target GC/MS concentrations. Each vial was tested six times by GC/MS analysis, and the average from these six replicate analyses was used as the final RDX concentration for the vial.

#### Ultraviolet/Visible Absorption Spectroscopy (UV/vis).

UV/vis absorption spectroscopy measurements were performed using a Shimadzu UV-1800 double beam spectrophotometer operated in photometric mode. Five point RDX calibration curves were made by taking aliquots from standard solutions containing the explosive in acetonitrile (Restek, Bellefonte, PA; Supelco, Bellefonte, PA; and Cerilliant, Round Rock, TX). The acetonitrile was evaporated, and the explosive residue was reconstituted in isobutyl alcohol and diluted to concentrations that spanned the instruments linear dynamic range for absorbance. Absorbance was measured using matched quartz cuvettes with a light path of 10 mm. One cuvette was filled with 1 mL of the explosive standard solution; the other functioned as a blank and was filled with 1 mL of isobutyl alcohol. Absorbance was then measured using wavelength scans from 230 to 300 nm.

**Ion Mobility Spectrometry.** Ion mobility spectrometry analyses were performed using the GC-IONSCAN 400B (Smiths Detection, Warren, NJ.) operated in the IONSCAN mode at a desorber temperature of 230  $^{\circ}\text{C}$ , a tube temperature of 114  $^{\circ}\text{C}$ , and a sampling time of 7 s. The instrument drift time is calibrated by means of an internal calibrant. All analyses were performed in the negative ion mode using hexachloroethane gas to produce the reactant ions.

## RESULTS AND DISCUSSION

To validate the inkjet printing process for quantity of explosive dispensed and process reproducibility, a test run through the entire printing process was performed using RDX as the explosive. Testing was performed over three consecutive days, allowing for the determination of both within-day and day-to-day reproducibility. RDX was selected because it is widely used in a variety of

explosives and is a major component of many plastic-bonded putty explosives. The remainder of this document discusses this RDX test run during which the following test materials were produced. (1) One hundred and thirty (130) trap samples for IMS testing and calibration. Ten traps were prepared at each of the following thirteen RDX quantities: 0.01, 0.05, 0.1, 0.5, 1, 5, 10, 15, 20, 40, 60, 80, and 100 ng. (2) Thirty (30) vials for the gravimetric and GC/MS determination of explosive quantity and inkjet printer reproducibility. Vials were printed at six different target concentrations for GC/MS analysis: 0.5, 1, 5, 15, 35 and 50  $\mu\text{g}/\text{mL}$ . Twelve vials were printed on day one (two at each target concentration), six vials on day two (one at each target concentration), and twelve vials on day three (two at each target concentration).

**Starting Solution Concentration.** The concentration of the starting inkjet printer solution was determined by gravimetry and verified by two additional independent analytical techniques: GC/MS and ultraviolet-visible (UV-vis) absorption spectroscopy. For gravimetry, an ampule containing 1 mL of standard RDX solution with starting concentration of  $1000 \pm 5 \mu\text{g}/\text{mL}$  was used. The solution was transferred to a previously weighed inkjet printer bottle (volume capacity 30 mL) that was then reweighed to determine the mass of solution transferred. The cap was removed, and the acetonitrile was allowed to evaporate. A measured mass of IBA (corresponding to 15.5 mL) was then added to the RDX residue to form the starting inkjet printer solution. From the manufacturers certified concentration value and gravimetric measurements, the starting concentration of the printer solution was determined to be  $64.4 \pm 0.3 \mu\text{g}/\text{mL}$  (assuming negligible loss of RDX during solvent evaporation). (Uncertainty represents propagation of errors resulting from the uncertainty in the starting solution concentration, the uncertainty in the balance readings, and the reproducibility of the balance.) Independent measurements of the concentration of this printer solution were determined by GC/MS and UV-vis spectroscopy to be  $62.9 \pm 0.3$  and  $62.8 \pm 0.2 \mu\text{g}/\text{mL}$ , respectively. (Uncertainty is the standard deviation from replicate analyses from a single sample.)

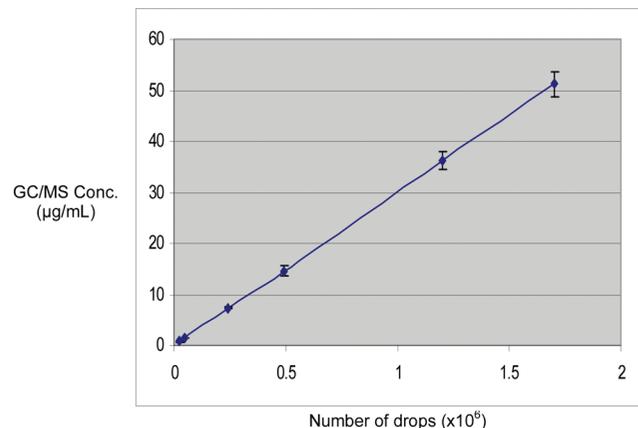
**Quantity of Explosive Dispensed by Inkjet Printer.** By determining the mass of RDX per dispensed droplet, we were able to produce test materials containing a range of different explosive quantities simply by printing different numbers of drops. RDX mass per drop was determined by dispensing preselected numbers of drops (2000 Hz) into GC bottles containing glass inserts for both gravimetric and chemical analyses. The number of droplets printed was selected to target six different concentrations for GC/MS analysis: 0.5, 1, 5, 15, 35 and 50  $\mu\text{g}/\text{mL}$ . After printing, the preweighed bottles were capped immediately and reweighed to determine the mass of the solution dispensed. Dividing solution mass by the specific gravity of IBA and multiplying this quotient by the concentration of the printer solution yields the mass of RDX dispensed by the inkjet printer. Dividing RDX mass by the number of drops dispensed gives the average mass of RDX per drop. Gravimetrically determined mass for the six different target concentrations is listed in Table 1.

Gravimetric determinations were verified by GC/MS. For GC/MS analysis, an internal standard was added and the inserts were filled with solvent (acetonitrile) to a final volume of 250  $\mu\text{L}$ . Analyses were performed and the concentrations are listed in

**Table 1. Comparison between Dispensed Mass of RDX Determined by Gravimetry and GC/MS<sup>a</sup>**

target GC/MS conc. ( $\mu\text{g}/\text{mL}$ )	actual GC/MS conc. ( $\mu\text{g}/\text{mL}$ )	dispensed RDX mass (GC/MS) <sup>b</sup> ( $\mu\text{g}$ )	dispensed solution mass (gravimetry) ( $\mu\text{g}$ )	dispensed RDX mass (gravimetry) <sup>c</sup> ( $\mu\text{g}$ )	difference <sup>d</sup> (%)	drops dispensed	RDX mass per drop (gravimetry) ( $\mu\text{g}$ )
0.5	$0.73 \pm 0.02$	$0.179 \pm 0.006$	$2.25 \times 10^3 \pm 3.9 \times 10^1$	$0.181 \pm 0.003$	1.3	24 317	$7.44 \times 10^{-6} \pm 3 \times 10^{-8}$
1	$1.44 \pm 0.03$	$0.351 \pm 0.006$	$4.55 \times 10^3 \pm 1.1 \times 10^2$	$0.365 \pm 0.009$	3.8	48 634	$7.51 \times 10^{-6} \pm 2 \times 10^{-8}$
5	$7.3 \pm 0.2$	$1.77 \pm 0.06$	$2.25 \times 10^4 \pm 8.9 \times 10^2$	$1.80 \pm 0.07$	1.8	243 170	$7.42 \times 10^{-6} \pm 2 \times 10^{-8}$
15	$14.6 \pm 1.0$	$3.61 \pm 0.19$	$4.56 \times 10^4 \pm 1.0 \times 10^3$	$3.66 \pm 0.08$	1.4	486 340	$7.53 \times 10^{-6} \pm 2 \times 10^{-8}$
35	$36.3 \pm 1.7$	$8.93 \pm 0.46$	$1.13 \times 10^5 \pm 3.1 \times 10^3$	$9.09 \pm 0.25$	1.7	1 215 851	$7.47 \times 10^{-6} \pm 2 \times 10^{-8}$
50	$51.2 \pm 2.5$	$12.66 \pm 0.58$	$1.59 \times 10^5 \pm 5.1 \times 10^3$	$12.79 \pm 0.41$	1.1	1 729 147	$7.40 \times 10^{-6} \pm 1 \times 10^{-8}$

<sup>a</sup> Dispensed mass values are averages from five different vials. Uncertainties are the standard deviation of the five measurements. The concentration values are the average from five different vials printed over a 3 day period. <sup>b</sup> Value is calculated by multiplying the GC/MS conc. by the volume of solution in the insert ( $\approx 0.250$  mL). <sup>c</sup> Value is calculated by dividing the dispensed solution mass by the specific gravity of IBA (0.8018) and multiplying this value by the RDX concentration of the printer solution ( $64.4$   $\mu\text{g}/\text{mL}$ ). <sup>d</sup> Value is calculated from the equation:  $(x_1 - x_2)/(x_1 + x_2)/2 \times 100$  where  $x_1$  = gravimetric concentration and  $x_2$  = GC/MS concentration.



**Figure 3.** Experimental calibration plot of the RDX concentration determined by GC/MS analysis versus the number of drops dispensed by the ink jet printer. Data points represent the average of five measurements. The uncertainty represents the standard deviation of the measurements.

Table 1. For comparison with gravimetric analyses, GC/MS analyses were converted to RDX mass by multiplying the determined concentration by the volume of solution in the insert ( $\approx 250$   $\mu\text{L}$ ). Comparison of the two techniques shows differences of less than 4% for all concentrations printed. The linear relationship between the number of drops dispensed and the RDX concentration determined by GC/MS analysis is plotted in Figure 3. Linear regression analysis of the data yields an  $r^2$  value of 0.99998.

**Potential Bias from Solvent Evaporation.** Gravimetric measurements are potentially biased by not considering the evaporation of isobutyl alcohol while printing into bottles. To investigate this bias, a comparison was done between the mass of solvent dispensed into preweighed bottles (as previously described) and the mass of an identical quantity of solvent dispensed into a bottle placed directly on the weighing pan of a microbalance. The microbalance was interfaced with a computer, and mass readings were recorded every 0.5 s. The evaporation rate was determined by dispensing solvent into the bottle and then monitoring the mass loss over time. Drop mass was determined by dispensing 50 000 drops into preweighed bottles that were then capped and reweighed to determine the mass of solvent dispensed. Immediately thereafter, 50 000 drops were dispensed into the bottle on the microbalance. The maximum balance reading was recorded as the mass of the 50 000 drops. This mass was corrected

**Table 2. Bias in Drop Mass Resulting from Not Correcting Gravimetric Results for Evaporation<sup>a</sup>**

drop mass (ng) (uncorrected)	drop mass (ng) (corrected for evaporation)	bias (%)
$90.0 \pm 0.2$	90.4	0.4
$89.8 \pm 0.2$	92.0	3.2
$93.2 \pm 0.2$	94.3	1.1
$92.5 \pm 0.2$	94.1	1.7
$93.5 \pm 0.2$	94.8	1.3
$90.9 \pm 0.2$	90.7	-0.3

<sup>a</sup> Bias is calculated by the formula:  $\text{Bias} = (x_2 - x_1)/x_2 \times 100$  where  $x_2$  = corrected mass,  $x_1$  = uncorrected mass. The uncertainty in the uncorrected drop mass results from the propagation of uncertainties in the balance readings divided by the number of drops printed.

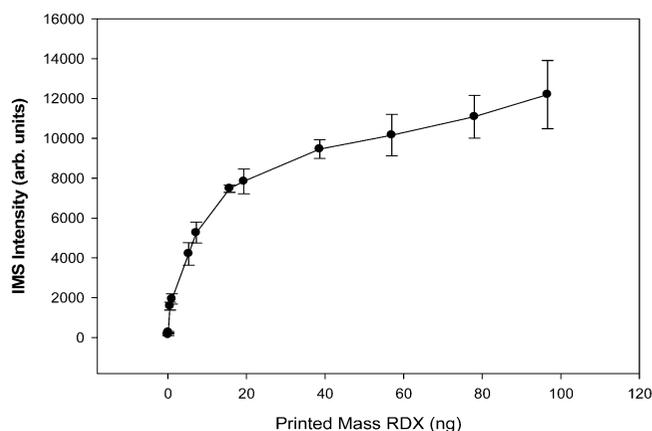
**Table 3. Gravimetric Analysis for Reproducibility of the Inkjet Printer**

day	no. analyses	gravimetry drop mass (ng)		
		average	standard deviation	% RSD
1	12	93.6	0.7	0.7
2	6	96.0	1.7	1.8
3	12	90.7	1.6	1.8
3 day total (combined result)	30	92.9	2.4	2.6

for evaporation and compared with the mass determined by printing into bottles (evaporation not considered). This procedure was repeated six times over an 8 h time period, and the results are recorded in Table 2. The average bias introduced by not considering evaporation in the mass measurements was determined to be 1.2%.

**Reproducibility.** The gravimetric data collected over the 3 day testing period was used to determine the reproducibility of the inkjet printer for producing trace level explosive materials. Within-day reproducibility was determined by analyzing drop mass data from the 12 bottles printed on day one and day three and the six bottles printed on day two. Day-to-day reproducibility was determined from drop mass calculations from all 30 bottles printed over the 3 day testing period. Results are summarized in Table 3. The within-day reproducibility for drop mass as measured by the percent relative standard deviation ranged from 0.7% to 1.8% whereas the day-to-day reproducibility was 2.6%.

**Inkjet Printed Samples and IMS Calibration.** The sample traps produced during the RDX test run were used to calibrate



**Figure 4.** Calibration of an IMS instrument (Smith's GC IONSCAN 400B) using inkjet generated test materials of RDX printed on treated filter paper substrates. Data points represent the average value of five measurements. Uncertainties are the standard deviation of these measurements.

the GC IONSCAN 400B IMS instrument (Figure 4). The detector response for this calibration shows classic IMS behavior displaying a linear range at low concentrations (0.05–15 ng) transforming to a second linear range of lesser slope at higher concentrations (15–100 ng).<sup>10,11</sup>

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## CONCLUSIONS

Explosives can be formulated into solutions that print reproducibly using piezoelectric drop-on-demand inkjet printing technology. Printer reproducibility was determined by gravimetric techniques to be better than 2% for within-day measurements and better than 3% for day-to-day comparisons. Gravimetry, GC/MS, and UV–vis absorption techniques were used to determine the quantity of explosive dispensed by the inkjet printer. Inkjet-printed trace level explosive test materials were used to calibrate IMS instruments at NIST. Explosive test materials are currently undergoing further field testing at several different federal agencies.

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## SUPPORTING INFORMATION AVAILABLE

Figure 1 showing three modes of printing. Figure 2 showing a sheet of inkjet printed explosive test materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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