

Investigating an Inkjet Printer for Standardized Sample Preparation

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ABSTRACT

Hazard detection systems must be evaluated with appropriate test material concentrations under controlled conditions in order to accurately identify and quantify unknown residues commonly utilized in theater. The existing assortment of hazard reference sample preparation methods/techniques presents a range of variability and reproducibility concerns, making it increasingly difficult to accurately assess optically based detection technologies. To overcome these challenges, we are examining the optimization, characterization, and calibration of microdroplets from an inkjet printer that has a proven capability for the preparation of energetic reference materials. Unlike other sample preparation methods that often result in the “coffee ring” effect, for which most of the material is concentrated along the edges, samples prepared using drop-on-demand inkjet technology demonstrate excellent uniform material dispersion throughout. Research presented herein focuses on the development of a simplistic printer calibration technique and sample preparation protocol for explosive materials testing based on drop-on-demand technology. Droplet mass and reproducibility were measured using ultraviolet-visible (UV-Vis) absorption spectroscopy. The results presented here demonstrate the operational factors that influence droplet dispensing for specific materials (e.g., energetic and interferents). Understanding these parameters permits the determination of droplet and sample uniformity and reproducibility (typical R^2 values of 0.991, relative standard deviation or RSD $\leq 5\%$), and thus the demonstrated maturation of a successful and robust methodology for energetic sample preparation.

Keywords: inkjet printing, drop-on-demand, explosives detection

1 INTRODUCTION

The development of systems capable of detecting and identifying explosive materials on surfaces at range is a priority for the United States Army. To properly assess detection and identification performance, emerging hazard detection systems must first be evaluated using calibrated samples under controlled conditions. Evaluation of systems based on optical detection techniques that allow for ranged sensing is complicated by spatial dependencies and a lack of a reliable means to generate calibrated reference samples containing the explosive materials. Therefore, standardized

reference materials and preparation methods are needed for proper testing of system capabilities, the establishment of reliable benchmarks for system development, and to compare technology between systems. Furthermore, an assortment of explosive reference materials is needed to allow for flexibility in reacting to the diverse range of threats encountered [1]. A variety of techniques that offer temporary alternatives has been employed, including spray deposition [2] and drop-and-dry (dropcasting) methods; however, it is often observed that there is material waste or uneven sample coverage. In the latter case, material loading fluctuations over a given surface area may result in significant signal variance from laser-based detection systems that have beam diameters on a similar length scale. Recently, drop-on-demand inkjet printing technology has emerged as an effective approach to produce test materials to meet the requirements for sample standardization [3-7]. Unlike other sample preparation methods that often result in the “coffee ring” effect, for which most of the material is concentrated along the edges, samples prepared using drop-on-demand inkjet technology demonstrate excellent uniform material dispersion throughout [3, 4, 8-11]. The uniformity achieved using inkjet printing is based on the distribution of a multitude of microdroplets over a defined area (i.e., an array of separated droplets). This is of particular concern with spatially sensitive techniques such as optical interrogation.

Piezoelectric drop-on-demand inkjet printing is an efficient approach for the deposition of microdroplets of solutions onto a surface [12, 13]. A range of deposited material concentrations can be achieved by varying the number and spacing of microdroplets printed. The reproducibility of optimized drop-on-demand systems has been reported to be better than 1% relative standard deviation (RSD) from measurement-to-measurement (within-day) and better than 2% RSD for day-to-day measurements of dispensed volumes [4, 14]. These deviations are significantly lower than those observed for other sample preparation methods.

Recently, we have utilized a common commercial off-the-shelf (COTS) drop-on-demand printing platform for the preparation of a variety of samples to be used in both laboratory and field tests for the assessment of the hazard detection capability of an optical detection system at range. This drop-on-demand platform has not been specially modified, and therefore results and conclusions should be applicable for standard instrument users. Here, we demonstrate the operational factors that influence droplet dispensing for energetic and interferent materials and the

development of this sample preparation method to produce test materials.

2 EXPERIMENTAL

2.1 Reagents and Materials

Ammonium nitrate (AN), methanol (MeOH), distilled water (H₂O), acetonitrile, sugar, urea, and potassium chlorate (KClO₃) were obtained from Sigma-Aldrich. 1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN) were obtained from Cerilliant. All inkjet printer stock solutions were prepared in a solution of methanol (MeOH) and water (v/v 2:1), acetonitrile (ACN), or water, depending on solubility. Cerilliant standards were packaged in ACN. All chemicals were used as received unless otherwise noted. All analyte solutions were dispensed at room temperature.

2.2 Inkjet Printing

Test materials were fabricated using a JetLab[®] 4 (MicroFab Technologies) tabletop printing platform. The system is shown in Figure 1(a). The JetLab[®] 4 is a drop-on-demand inkjet printing system with drop ejection drive electronics (JetDrive[™] III), a drop visualization system, and precision X, Y, Z motion control. The standard manual pressure controller (Fairchild[®]) was upgraded with a COTS electronic pneumatic pressure controller (MicroFab). The dispensing device (print head assembly, MJ-AL-01-060) consists of a glass capillary tube with a 60 μm diameter orifice coupled to a piezoelectric element. Photographs of the dispensing device encasement and the print head assembly are shown in Figures 1(b) and 1(c), respectively. Both sinusoidal waveform voltage pulses and standard waveform bipolar voltage pulses were used to generate microdrops.

Determining optimal jetting parameters requires trial-and-error. Stable droplet ejection is achieved by visually observing expelled microdrops and adjusting voltage pulse parameters and capillary fluid backfill pressure to create an “ideal” drop. Drops are visualized using synchronized strobe illumination and a charged coupled device (CCD) camera. Printing was performed at a frequency of 250 Hz. Drop diameter was estimated to be ~60 μm, based on the capillary orifice diameter. An optimal drop is a droplet typically equal in size to the dispensing orifice being used, which does not have satellites, and consistently falls at an optimum velocity of ~2 m/s. Satellites are secondary droplets, ejected following the optimal droplet, typically observed to be smaller in volume than the optimal droplet. Satellites deposited add to the total concentration error and can affect droplet spacing uniformity.

During printing, a single substrate or vessel was placed on the sample stage. The print head remained fixed at a specified height while the stage moved to print a specified

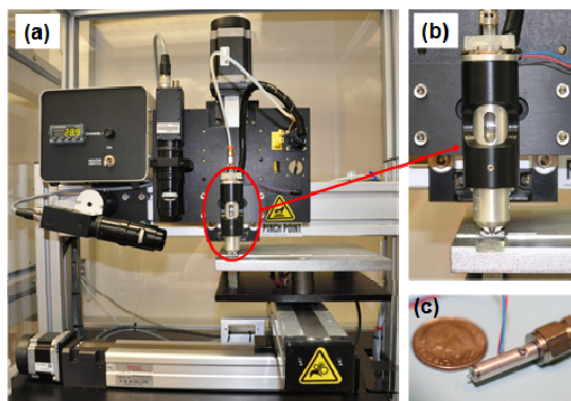


Figure 1: Photographs of (a) JetLab[®] 4 drop-on-demand inkjet printing platform; (b) dispensing device and ink solution encasement; and (c) print head assembly.

pattern or number of microdrops. A rectangular area, which covers a substrate region with rows and columns of equidistant points, was pre-programmed based on the vessel size. The total number of drops needed to achieve a desired concentration per unit area is calculated based on the volume of a single microdrop and the solution concentration. Based on the number of total drops needed, the array spacing and drops needed per line can be calculated. These values are easily adjusted depending on solution concentration. Patterns were printed using the print on-the-fly mode. In this mode, the stage moves continuously without stopping as a single microdrop is dispensed at each array element. Sample throughput is improved in print on-the-fly mode.

2.3 UV-Vis Absorption Spectroscopy

UV-Vis absorption spectroscopy measurements were collected using a Shimadzu[®] UV-3600 UV-VIS spectrophotometer. Calibration curves were constructed by measuring the absorbance spectra from standard solutions (of known sample concentrations) containing various pre-determined energetic and interferent compounds. The evaluated analytes were: AN, potassium chlorate, HMX, TNT, RDX, PETN, urea, and sugar. The analyte of interest was dissolved in the appropriate solvent and then diluted to various concentrations. Absorbance was measured using quartz cuvettes (1 cm path length) in a dual beam UV-Vis. One cuvette was filled with 3 mL of analyte solution (sample), and the other was filled with 3 mL of pure solvent (blank, H₂O). Wavelength scans from 190–400 nm were used to measure the absorbance of the various target materials at known concentrations. The analytes of interest had absorption features in this wavelength region. Data analysis was completed using UV Probe software (version 1.10).

3 RESULTS AND DISCUSSION

We report microdroplet optimization results for a 60 μm orifice dispensing device with analyte samples in conjunction with ACN, 2:1 MeOH:H₂O, and H₂O solvents. We also discuss the performance for the microdrop mass calibration method described, as applied to selected inkjet stock solutions. These results also include the determined repeatability and standard uncertainties of the experimental measurements.

3.1 Microdroplet Optimization

Prior to analyte deposition, it was important to have a working knowledge of how the drop-on-demand instrument settings, analyte concentration, and inkjet printing solvent viscosity (which can also be a function of analyte concentration), influence the character of droplets produced. Many variables impact the drop; therefore, optimized parameters are needed to achieve the best drop at a sufficient velocity. Controlling the physical properties (e.g., size, volume) of the dispensed microdrops will ultimately also affect droplet variation and reproducibility. The volume of the dispensed microdroplet is a function of the printing fluid, dispensing device orifice diameter, and waveform parameters. In all cases, under the conditions tested, it was found that in order to maintain a consistent drop with an appropriate velocity, several waveform variables needed to be optimized. In general, H₂O-containing solvents produced visually larger droplets (in flight). Larger droplets were also visualized when sinusoidal waveform parameters were used to generate microdroplets. Parameters were determined for the analytes of interest in suitable solvents and have been reported previously [15]. These parameters were uniquely capable of producing consistent drops within-day and day-to-day.

3.2 Microdroplet Mass Determination

To determine the mass of analyte contained in each ejected microdroplet, absorption spectra were recorded for known concentrations of the analyte. A calibration curve was constructed using these concentrations and absorbance spectral peak areas calculated by the instrument software and based on the specified wavelength range. Calibration curves were used to prepare linear regressions from which the microdroplet mass and standard error could be calculated using the equation of the line and goodness of fit value (R^2 value). The solutions used to construct the calibration curves were independent from the solutions used in the drop-on-demand inkjet printer for droplet mass determinations. Calibration curves for the evaluated analytes have been previously reported [15].

The mass of each analyte of interest deposited per drop was determined by dispensing known numbers of drops into a Petri dish containing a known volume of solvent. Spectral peak areas for these droplets in solution were determined from the UV-Vis absorbance spectra. These y

values were then substituted into the respective calibration curve equation ($y = mx + b$) to determine solution concentration. Based on this concentration, volume of solvent and total number of drops dispensed, the mass of a single droplet could be calculated. For example, considering the AN peak area from 262 nm to 340 nm, the linear fit equation for the AN calibration curve is $y = 222.12x - 0.0052$. Based on the peak area for an unknown printed sample of AN (15 arrays printed into 3 mL of H₂O, 8,464 drops per array), the predicted concentration from the calibration curve equation is 2.94×10^{-3} M AN. The following calculations were completed to determine the mass of AN in a single microdrop. Masses were calculated in μg as test sample concentrations are calculated and prepared in $\mu\text{g}/\text{cm}^2$.

- (1) $2.94 \times 10^{-3} \text{ mol/L} \times 0.003 \text{ L} = 8.83 \times 10^{-6} \text{ mol}$
- (2) $8.83 \times 10^{-6} \text{ mol} \times 80.052 \text{ g/mol} = 7.07 \times 10^{-4} \text{ g AN}$
(total mass)
- (3) $7.07 \times 10^{-4} \text{ g AN}/126,960 \text{ drops} = 5.57 \times 10^{-9} \text{ g AN/drop}$
 $\text{AN/drop} = 5.57 \times 10^{-3} \mu\text{g AN/drop}$

This methodology was repeated at least three times per run, and resulted in excellent RSD values of $\leq 10\%$ using the bipolar waveform (e.g., 0.87% and 9% RSD for AN and KClO₃, respectively) and $\leq 8\%$ using the sinusoidal waveform (e.g., 3% and 8% RSD for RDX and PETN, respectively). RSD values $\leq 10\%$ were sufficient for the preparation of samples and calibration was not repeated over the course of a typical sample set preparation; however, calibration was repeated before starting a new sample set. RSD values for long term (i.e., months) stability of microdroplet mass were typically $\leq 15\%$. Microdrop mass averages and RSD values were determined by averaging at least three successive additions of a single array to a known solvent volume. These values for all of the energetic analytes of interest have been previously reported [15]. The sinusoidal waveform parameters produced a larger droplet mass compared to the bipolar waveform parameters; however, there was no significant (i.e., orders of magnitude) increase in overall deposited analyte mass.

3.3 Printing Parameters

By determining the mass of material dispensed per droplet, test materials containing a known range of sample concentrations were successfully produced. Based on the desired sample area and analyte concentration within that area ($\mu\text{g}/\text{cm}^2$) to be printed, the total number of microdroplets needed to cover the area and the droplet spacing could be calculated. The following calculations were completed to determine these printing parameters for a $25 \mu\text{g}/\text{cm}^2$ sample of AN having a sample area of 25.8 cm^2 (2580 mm^2).

- (1) $(25 \mu\text{g}/\text{cm}^2 \times 25.8 \text{ cm}^2)/(5.57 \times 10^{-3} \mu\text{g AN}/\text{drop}) = 1.16 \times 10^5$ total drops needed
- (2) $\sqrt{(2580 \text{ mm}^2/1.16 \times 10^5 \text{ total drops})} = 0.149 \text{ mm}$ spacing between drops
- (3) $50.8 \text{ mm sample length}/0.149 \text{ mm spacing} = 34$ drops per row (lengthwise, y)
- (4) $50.8 \text{ mm sample width}/0.149 \text{ mm spacing} = 34$ drops per row (widthwise, x)

The spacing and number of drops per row in each direction were used with the drop-on-demand inkjet printer software to print an array. Similar calculations were made to determine microdroplet spacing and drops per row for additional areal concentrations and the other energetic analytes of interest. In order to maintain separation of droplets on the sample substrate, the space between droplets is limited by the solution behavior (e.g., evaporation rate, surface tension) once a microdroplet is deposited onto the substrate. This spacing limitation is important in relation to the type of optical detection technology being assessed using this sample preparation method. The dimensions of the interrogating beam area must be considered to ensure the areal concentration is uniform.

4 CONCLUSIONS

Our results demonstrate a sample preparation protocol that produces uniform samples to be used for utility assessments of emerging optical hazard detection technologies. This method for determining the mass of material contained in droplets ejected from a drop-on-demand inkjet printer allows for system calibration and the preparation of specific sample material mass loadings. Based on this report, we consider the use of a COTS drop-on-demand system in combination with our analysis and validation techniques to be a reasonable method for the fabrication of standardized reference energetic and interferent test materials, and should be considered a predominant and universal innovative industry standard. However, further investigations into analyte polymorphism and long-term sample stability are needed.

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