Depositing Explosives and Chemical Materials on Relevant Surfaces using Inkjet Technology for Calibration Test Standards

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ABSTRACT

Edgewood Chemical Biological Center (ECBC) is leading an inter-agency working group, to expand chemical inkjet printing techniques, and to fabricate surface standards in a controlled, uniform and quantifiable fashion, for the evaluation of stand-off active and passive optical systems [1]. The Direct Jet 1309 printer (Direct Color Systems, Rocky Hill, CT) was used to generate the modeled distribution of actual chemicals on relevant surfaces. Various chemical simulant characteristics were evaluated for printing suitability. These characteristics included viscosity, surface tension, density, substrate surface energy, and harmfulness to the printer. Quantitative analyses were performed on printed materials. Results showed that the printer produced uniform distributions as well as quantitatively accurate samples within 7% of the predicted amount. When samples were printed on a heated substrate, particles were much smaller and more evenly distributed than at room temperature. The Automated Aerosol Sprayer provides the ability to deposit higher concentrations.

Keywords: inkjet, optical standards, calibrated standards, surface standards, explosives, chemicals

1 BACKGROUND

Materials deposited on manmade or natural surfaces are frequently utilized as calibration standards for chemical or biological detecting systems. To determine threshold sensitivity of systems which detect chem/bio agents and explosives, precise accurate quantities must be deposited. Present drop-and-dry deposition systems produce a largely non-uniform distribution of particles with an overall sample spread shape and area that is difficult to control or predict. Imaging sample of drop and dry in Figure 1 shows coffee ring effect which leads to inaccurate optical detection [2].

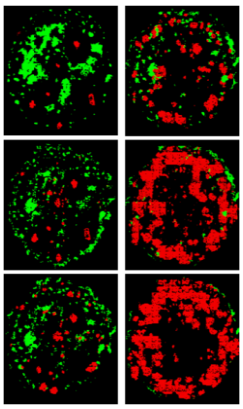

Figure 1. Coffee ring effect

2 INKJET PRINTER OVERVIEW

The Direct Jet 1309 flat-bed inkjet printer (Figure 2) is presently used to deposit various chemicals on surfaces, such as substrates of aluminum and Teflon as well as microscope slides. Concentrations of substrates from 1 to100 µg/cm² are deposited in a single pass, and increased amounts use multiple coatings. The Direct Jet 1309 inkjet color printer is based on an Epson design using Epson style cartridges and an Epson print head (Figure 3). The printer is supplied with eight empty ink cartridges that may be filled with ink, or in this case, chemicals to be deposited.

2.1 Direct Jet 1309 Printer Characteristics

Prints directly on concrete, metal, glass, plastic, etc.;
Maximum substrate size, 13 × 9 × 2 in.;
Maximum substrate weight, 10 lb;
Resolution range, 720 to 5760 dpi;
Droplet size, 1.5 to 21 pL;
Print head hole diameter is approximately 23 µm with 140 µm Spacing.

Figure 2. Direct Jet 1309 inkjet printer.

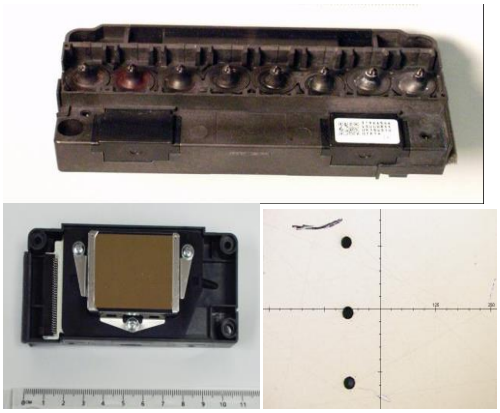

Figure 3. Epson print head technology.

2.2 Suitable Liquids

Ink target viscosity range is from 1.5 to 5 cP. This is the usual viscosity range for printer inks. A suitable liquid is SF96-5, which is a low-surface tension polydimethylsiloxane fluid that is commonly used as a base fluid in personal care products. SF96 is a clear liquid with a distinct, recognizable Raman signature that makes it a suitable liquid chemical agent simulant. The viscosity of SF96-5 is 5 cP, which is comparable to printer ink. One disadvantage in printing with SF96 is its low surface tension of 19.7 dynes/cm, which causes complete wetting on high surface tension, free-energy materials such as metal and glass. However, a suitable substrate material is PTFE (Teflon) on which printed patterns of SF96-5 show very little spreading. Specifications for SF96-5 and Teflon at 25 °C are as follows:

- SF96-5 specific gravity: 0.913
- SF96-5 surface tension: 19.7 dynes/cm
- SF96-5 viscosity: 5.0 cP
- Teflon surface free energy: 20.0 dynes/cm

To print dry chemicals, a number of solvents have been used. These solvents include ethanol, acetonitrile, water, and water–alcohol mix. Viscosities up to 5 cP have printed well; however, surface tension has proven to be of greater concern than viscosity. The surface tension of most water-based inks is 34–40 dynes/cm. If surface tension is too high, the ink may not wet or travel through the ink cartridge correctly.

The print-head hole diameter measures approximately 23 µ, which may also influence the passage of solvent through the cartridge. The use of water as a chemical solvent initially caused printing problems in the 1309 printer. Water surface tension is 72.8 dynes/cm, which is high enough to prevent water from passing through some holes in the print head, resulting in missed printed lines, insufficient solute volume, and, in some cases, the entire absence of any printing. The addition of a small amount of surfactant (Tween 20) to the water completely eliminated this problem. As little as 0.05% Tween-to-water mix has proven sufficient. As of this date, the Raman chemical spectra of Tween has not been found to interfere with the desired spectra of the chemicals deposited. It should be noted that to prevent blocking the fine holes in the print head, all printing liquids are filtered to 1.0 µ.

2.3 Print Procedure

A number of tests are required to determine how various printer settings and chemical parameters affect the chemical mass deposited. Printer settings include resolution, drop size, drop volume, number of coats, maximum ink, and number of print cartridges used. Chemical parameters include viscosity, surface tension, and density. Chemicals may be liquid or a solid dissolved in suitable solvent. The volume per droplet may be specified in the printing program as 7, 14, or 21 pL; however, these volumes were determined using printer ink, were not necessarily accurate for the chemicals to be deposited, and had to be reevaluated.

Determination of actual chemical mass deposited required a number of steps. Initially, the substrate was to be weighed before and after chemical deposition. In practice, however, this procedure is not always practical because the anticipated chemical mass may be in the milligram or microgram range, and the background substrate may be weighed in grams. In these cases, the resolution of the available laboratory scale may provide inadequate results. Initially, the procedure used for determining the chemical mass deposited on a heavy substrate is to use a small lightweight aluminum substrate to determine the droplet volume. This may be accomplished by weighing the substrate before printing and again after the substrate is dried using a heat gun. With knowledge of the chemical concentration of the liquid, the droplet volume may be calculated. Some chemicals used for printing, such as ammonium nitrate, are very hygroscopic and care must be exercised when weighing the substrate. Weight will initially decrease as the substrate is dried. The weight then increases as moisture is absorbed by the chemical from the air. The weight eventually stabilizes as the chemical moisture content approaches that of the air. This stabilized weight measurement probably introduces the least experimental error by assuming that the chemical moisture content at the time of

this measurement is similar to the moisture content when the chemical was first dissolved.

Equations 1 through 4 are useful chemical deposition formulas. The constant *K*, which appears dimensionless, was derived to simplify calculations by allowing numerical values to be used for droplets in picoliters, area in square centimeters, and concentrations in grams per liter. The value of *K* is determined by droplet area, which varies with printer resolution or dots per inch (dpi).

$$C = (S \times K)/P \quad (1)$$

$$P = (K \times M)/(A \times C) \quad (2)$$

$$M = (P \times A \times C)/K \quad (3)$$

$$S = M/A \quad (4)$$

Where:

A is surface area (cm²);

P is droplet (pL);

C is liquid concentration (g/L);

K is 9.775E+6 (for 720 dpi), *K* is 2.44E+6 (for 1440 dpi);

M is mass deposited (g); and

S is surface concentration (g/cm²).

2.4 Printing on a Heated Substrate

When printing aqueous solutions of chemicals with the Direct Jet 1309 printer, the dried chemical crystal residue patterns exhibit significant voids. Although printing may be set at 720 dpi, the crystal patterns may be as sparse as 150 crystals per inch. This may be attributed to the fact that the printer droplets do not dry instantly as they hit the substrate, and the puddles that form join together to grow larger crystals as the solvent dries. It has been observed that when similar chemical solutions are paint-sprayed onto a hot (70 °C) substrate, the crystals are smaller, more numerous, and more closely spaced. To facilitate printing on heated substrates, a temperature-controlled hotplate was designed and installed on the printer bed. Substrate temperature is maintained at 80 °C. Figure 4 shows photographs of potassium chlorate crystals deposited with and without heating. Both photographs are at the same scale.

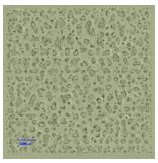

Figure 4. (left) $KClO_3$, no heating, 54 µg/cm² ((right) heated to 80 °C, 45 µg/cm²

3. QUANTIFICATION ANALYSIS

3.1 Energetic Print Testing of 3× 3 in. Aluminum Panels

For ground truth, the density of coupon deposition was verified using several methods including theoretical calculation, coupon mass measurement, and chemical laboratory analysis.

A 2 × 2 in. pattern of ammonium perchlorate (APC) was printed on 3× 3 in. aluminum panels (Figure 5).

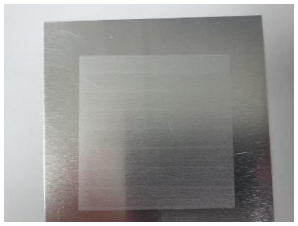

Figure 5. The 3 × 3 in. aluminum sample panel.

3.2 Calculation

The printed mass is calculated by first determining the solution concentration for the desired deposition. For example, for a 50 µg/cm^2 surface concentration, we can calculate a solution concentration (g/l) using eq 5.

$$C = (S \times K)/P \quad (5)$$

Where:

S is 50E–6 g/cm^2,

K is 9.775E+6 (720 DPI),

P is 14 pL/drop, and

C is 34 g/L.

The total printed mass is then calculated using eq. 6

$$M = (P \times A \times C)/K \quad (6)$$

Where

P is 14 pL/drop,

A is 25.81 cm^2,

C is 32 g/L,

K is 9.775E+6 (720 dpi), and

M is 1.2 mg.

3.3 Verification

Table 1 shows the results of all the samples that were sent to the laboratory for verification using the extraction method described in Section 4.1.4. The overall average difference of the verification results (VR) when compared with the coupon mass measurement was only 7%.

Sample Size (µg/cm2)	Calculated (mg)	Printed Amount (Measured mg)	VR (mg)	|VR – Measured| /VR (%)
50	1.29	1.41	1.65	15
65	1.68	1.67	1.60	5
59	1.52	1.53	1.56	2
54	1.39	1.39	1.38	1
47	1.21	1.21	1.39	13
50	1.29	1.30	1.21	7
60	1.55	1.57	1.21	29
101	2.61	2.61	2.79	7
101	2.61	2.61	2.83	8
53	1.37	1.37	1.35	1
100	2.58	2.60	3.09	16
51	1.32	1.31	1.34	2
49	1.26	1.27	1.39	9
111	2.86	2.87	2.92	2
			Average	7

Table 1. Comparison of VR to Measured and Calculated Values.

3.4 APC Extraction Method

Five Ziploc brand, plastic polypropylene (PP) containers were obtained and rinsed by pipetting 40 mL of deionized (DI) water into the containers. The surface of each aluminum panel was rinsed ~25 times by adding the same solvent (DI water) into the containers until no APC could be seen on the panel surface. The aluminum panels were then placed face down into the plastic containers, and the lids were snapped on. All five containers were then placed onto an orbital shaker table and allowed to shake at a low speed (~100 rpm) for ~18 h.

A 500 µL aliquot of sample was removed from each plastic container using an automatic pipette (set at 500 µL). The samples were placed into separate, labeled, plastic autosampler vials and submitted for ion chromatography (IC)-Conductivity Detection (CD) analysis. Most of the remaining sample extracts (~20.0 mL) were transferred to 20 mL plastic bottles and stored in the refrigerator at ~8°C.

The following information was used to make the calculations in this study:

- APC (NH_4ClO_4) = 117.493 g/mol
- Ammonium (NH_4^+) = 18.042 g/mol [15.36% of APC]
- Perchlorate (ClO_4^-) = 99.451 g/mol [84.64% of APC]

4. SUMMARY

Deposition of chemical samples on relevant surfaces using the Direct Jet 1309 flat-bed inkjet printer produced uniform distributions as well as quantitatively accurate samples within 7% of the predicted amount. When samples were printed on a heated substrate, the particles were much smaller and more evenly distributed than when printed at room temperature.

REFERENCES

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