Preparation of Trace Explosives Standards by Advanced Inkjet Printing

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Abstract

Accurately defined test samples of explosive materials on different substrates, precise in amount and sample coverage, are critical for evaluating the performance of existing sensors and predicting the performance of future detection capabilities.

Drop-on-demand and inkjet printing technology has become a promising method of producing standardized chemically contaminated test materials with high precision, accuracy, scalability and flexibility to allow for the inexpensive high-throughput production of test materials for the evaluation of stand-off sensors. Since more than ten years Fraunhofer ICT has been using a GeSiM Nano-Plotter NP 2.1 to produce test samples of explosive materials on different substrates in several national and European projects, among them NATO STANDEX, NATO SET-237 and NATO DEXTER. Currently, the work is continued within the NATO Task Group SET-316 "Realistic Trace Explosives Test Standards for Evaluation of Optical Sensors in Relevant Scenarios" and the EU H2020 Project RISEN.

The Poster will show examples of printed samples and describe the methods of quality control regarding the accurate mass loading as well as the uniform surface coverage and morphology of the deposits.

Introduction

Accurately defined test samples, precise in amount and sample coverage, are critical for evaluating the performance of existing sensors and predicting the performance of future detection capabilities. An assortment of reference materials is also needed to allow the required flexibility to react to the diverse and evolving range of threats encountered. Therefore, the development and adoption of standardized methods for the evaluation of standoff optical systems for explosive and chemical detection is needed. Existing preparation methods of reference samples, such as drop-and-dry (drop casting) methods, present a range of variability and reproducibility issues, including inhomogeneous sample coverage and material waste. Drop-on-demand and inkjet printing technology has become a promising method of producing standardized chemically contaminated test materials with high precision,

accuracy, scalability, and flexibility to allow for the inexpensive, high-throughput production of test materials. War fighters continue to ask for the capability to detect Improvised Explosive Devices (IEDs) from a safe distance. Without well-qualified and verified standards, it is impossible to provide adequate confidence on the performance of sensors.
For more than a decade, Fraunhofer ICT is working with a drop-on-demand printer to prepare test samples of energetic materials on various substrates in several national and international projects among them NATO STANDEX, NATO SET-237 and NATO DEXTER. Currently, the work is continued within the NATO Task Group SET-316 “Realistic Trace Explosives Test Standards for Evaluation of Optical Sensors in Relevant Scenarios” and the EU H2020 Project RISEN.

Deposition of energetic material on surfaces

Inkjet printing is used in order to create standardized and defined samples for training and evaluation of trace and optical detection systems. By means of an inkjet printer, controlled and specified loadings (mass per surface) of different materials (explosives, precursors, HMEs and others) can be deposited on a range of substrates (natural, manmade, fabrics, plastics, metals, glass). In the course of the inkjet printing, one or more micro drops of a concentrated solution of an explosive material are dispensed at specific locations of the substrate. In the beginning, the deposited liquid droplets form spherical caps, while after the evaporation of the solvent, solid particles remain on the substrate surface. Sequential translation of the printer stage can lead to various arrays of solid particles.

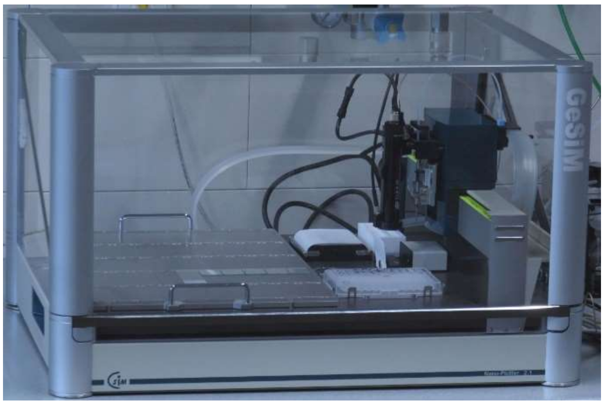


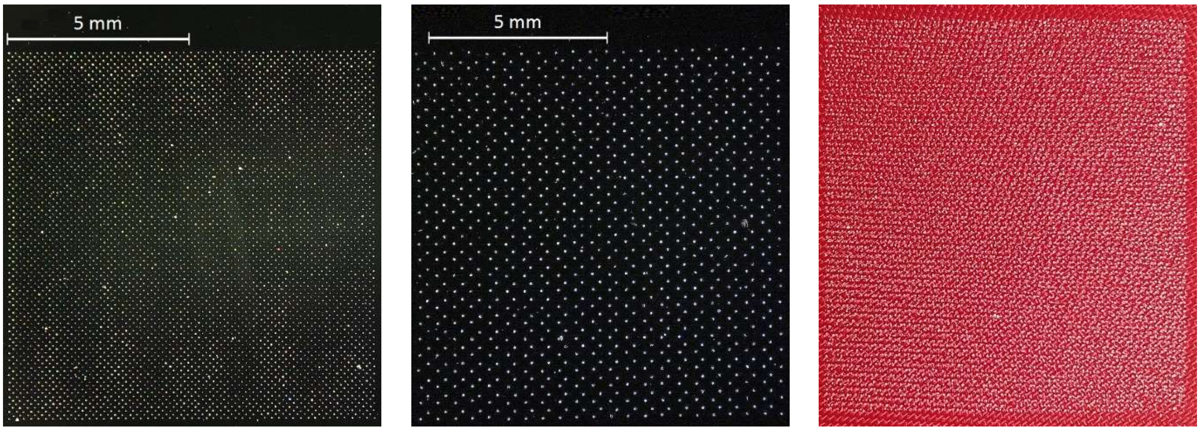
Figure 1 GeSiM Nano-Plotter NP 2.1 at ICT laboratory

Fraunhofer ICT uses a GeSiM Nano-Plotter NP 2.1 equipped with on single piezo-pipette delivering one or multiple droplets of about 300 pL that can be located by the x-y-z-motion control with an accuracy of 10 µm. The loading can be specified by adjusting the pipetting parameters (droplet volume, number of droplets per spot, spots per area) and by variation of the concentration of the printing solution.

The droplet volume is measured automatically before and after each printing run by an optical microscope and a flow sensor.

Each printed sample is evaluated by optical microscopy using a Leica DM750M-microscope and a Leica S9D macroscope, both equipped with a camera system.

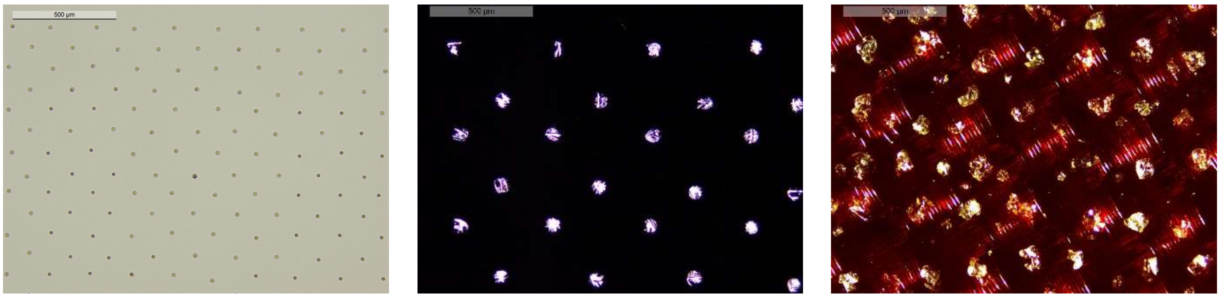
In our various projects Fraunhofer ICT printed samples of most military explosives, pyrotechnics and many others in loads reaching from a few Nanograms (ng) per cm² up to 1000 µg/cm² on different substrates. Figure 3 shows macroscopic pictures of printed samples with loads from 500 ng/cm² to 500 µg/cm².



$KClO_3$ 500 ng/cm² on Aluminium 10x10 mm	HMX 10 µg/cm² on Aluminium 10x10 mm	KNO_3 500 µg/cm² on Polyamide-fabric 20x20 mm

Figure 2: Macroscopic pictures of printed samples

The same samples are shown in higher magnification as microscopic pictures in Figure 3.



$KClO_3$ 500 ng/cm² on Aluminium	HMX 10 µg/cm² on Aluminium	KNO_3 500 µg/cm² on Polyamide-fabric

Figure 3: Optical microscopic pictures of the same samples, (scalebar 500 µm each)

In most projects rectangular plot-patterns were printed, but the Nano-Plotter is also capable of printing any other pattern converting arbitrary bitmap graphics in a corresponding plotting pattern. Figure 4 shows the bitmap of the original fingerprint (200 dpi) and the macroscopic picture of this fingerprint plotted on black ABS from KNO_3-solution in water c=10 mg/ml, 5130 spots, 1 droplet/spot. The total load was 17.2 µg what corresponds to an area-related density of 4.78 µg/cm².

Figure 4: left: Bitmap of a fingerprint, right: result of the printing plotted with KNO_3

Quality control of the printed samples

QC-samples for quantification are printed frequently on glass or aluminium and their actual load is determined using liquid (HPLC-DAD, IC) or gas chromatography (GC-MS) after quantitatively washing the residues from the substrates. The quantification by HPLC and GC-MS can be used if the total printed amount is above approximately 100 ng, for IC above 500 ng. For lower loads, a different approach is necessary. In these cases, the QC-samples are printed directly to the swabs of our IMS, a Bruker DE-tector. These printed swabs are analysed after evaporation of the solvent by thermodesorption of the total load into the detection chamber of the IMS. Depending on the substance the detection limit of the IMS is between 1 and 15 ng.

The mass accuracy in serial plots was determined to be between 1 – 5 %.

In the NATO-SET-237 “Printed Standards for Standoff Detection” an additional quality control of the printed samples was established. It is based on particle analysis performed on microscopic pictures of the samples. Micrographs were processed with ImageJ, an open-source image-processing program designed for scientific multidimensional images, which has already been applied to the analysis of particles in various research areas and for different materials. ImageJ is a Java-based image processing program developed at the National Institutes of Health (NIH) and the Laboratory for Optical and Computational Instrumentation (LOCI, University of Wisconsin). One of the steps that is required during the processing of images is the selection of the threshold function to convert grayscale or colour images into binary images, which will keep only information about the particles while unwanted background information is removed.

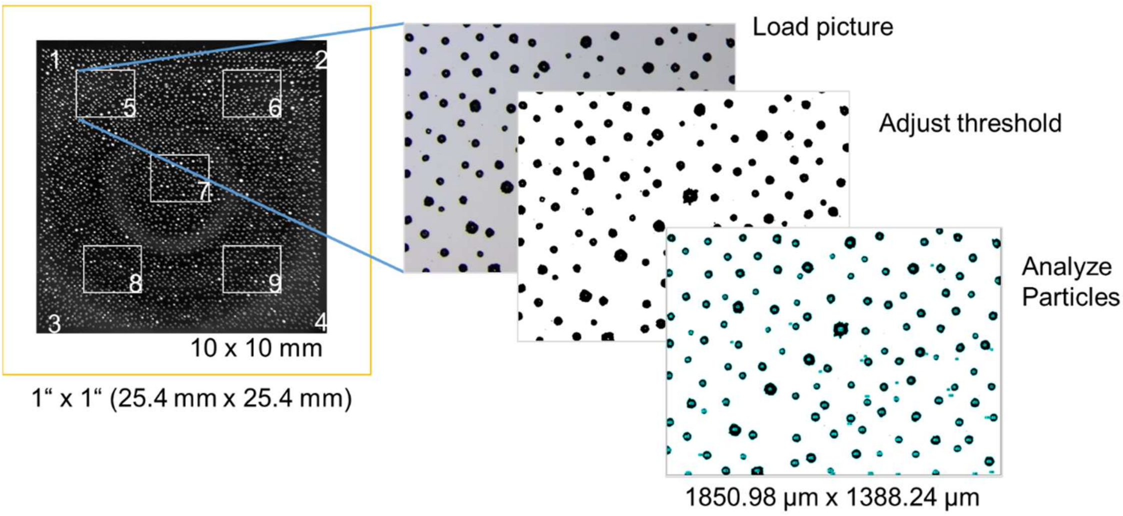


Figure 5 Optical microscopy and particle analysis done with ImageJ

The applied threshold value defines which pixels are included in the definition of the particle and, consequently, affects all the particle parameters. The choice of the threshold value depends upon the background colour and brightness of the particle to be identified in the image. Threshold values can be set automatically or interactively to segment the image into features of interest (particles) and background. Manual methods have several limitations like no/low reproducibility, high operator bias, it is tedious and time-consuming to find the better cut-off value, incompatibility with automatic processing, high intra- and inter-user variability. The manual selection of the threshold is always dependent on the knowledge and experience of the scientist who is processing the images. A fixed manual threshold could be chosen and then applied to all images to meet the criterion to treat equally all the images, but the comparison at the end may not be possible in presence of a certain variability in the samples from the same laboratory and generally even higher variability from samples prepared by various laboratories using different methodologies. At least it was decided to apply several algorithms available in ImageJ to automatically apply a threshold based on image-intrinsic properties. For images of explosives particles on Al-coated slides some automatic threshold methods perform better than others but, generally, the same algorithm cannot be applied to all images acquired from samples prepared using different energetic materials or produced by different laboratories.

The group developed a plugin for ImageJ where all the available automatic thresholding methods are applied to the images, and the important parameters, such as the surface coverage and the particle size distribution are calculated for all algorithms. After excluding the outliers, the algorithms leading to the minimum, median and maximal values are applied on the pictures again to calculate and display the particle size distribution. An example for such calculation is shown in Table 1 for a sample of RDX, 1 $\mu g/cm^2$, printed on aluminium coated glass.

Table 1 Summary of particle calculation for a sample of RDX 1 $\mu g/cm^2$

Threshold selection		Gray value	Surface coverage (%)	Size (µm) / Percentile (%)					Relative Span
				10	25	50	75	90	
Minimum	*Minimum*	*105.2*	*0.38*	**2.28**	**12.16**	**12.66**	**12.90**	**13.18**	**0.86**
Median	*IJ_IsoData*	*145.2*	*0.42*	**1.44**	**2.70**	**13.22**	**13.53**	**13.80**	**0.93**
Maximum	*Triangle*	*229.0*	*0.80*	**1.02**	**1.02**	**1.02**	**1.44**	**3.23**	**2.16**

Summary

Drop-on-demand-printing of explosives is approved to be a useful method for the preparation of test materials for optical sensors, which are accurate in mass loading and surface distribution. Furthermore, the morphology of the particles can be controlled by adjusting the printing parameters. Single deposits tend to deliver more amorphous particles, printing several runs on the same spot allows for more crystalline particles. One known problem occurs when printing RDX, where the remains after evaporation of the solvent tend to stay in the metastable α-configuration, while RDX bulk material shows the stable β-Form. These polymorphs differ in their IR- and Raman-spectra, which has to be considered in the libraries of the spectral sensors.