Interactions of Polymers and Energetic Materials

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INTERACTIONS OF POLYMERS AND ENERGETIC MATERIALS

BY

REBECCA M. LEVINE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER

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THESIS

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2017
ABSTRACT

Trace explosive detection is the primary way for quick and easy sampling of various surfaces in a check-point environment, e.g. an airport. The swabs used for commercial explosive detectors, such as ion mobility spectrometers, are made of various materials. The difficulty in collection and analysis of explosive traces is that the swabs must be effective at adsorbing as well as desorbing materials, i.e. pickup from the surface and release into the detection device. This dichotomy results in a tradeoff for development of new swabs. Generally, desorption is considered to be the more desirable property; therefore, Teflon is one choice for commercial swabs. It would be ideal to develop a swab with both enhanced adsorption and desorption. One way to accomplish this is to apply an electrostatic charge to commercial swabs. This enhances their attraction to explosive particles, but once the swab is placed in the inlet of commercial detection instrument, the charge is dissipated, and desorption of the particles into the instrument proceeds as usual.

Methods of generating electrostatically charge swabs was determined; triboelectric charging vs corona charging was compared examining magnitude of the charge, reproducibility and stability, and effects of humidity. The magnitude of charge necessary for enhanced collection of particles was evaluated using an electrostatic voltmeter to measure charge and various means to measure particle pickup. Corona charging was determined to be more effective. Enhancement of collection was judged by comparing results of corona charging swabs to those achieved by contact swabbing. Two variables were examined: the analyte and the substrate from which the analyte is removed. The swab material was Nomex. In each case but three, collection of an
analyte by an electrostatically enhanced swab outperformed the traditional contact swabbing. Evaluation was determined by a rigorous quantification by mass spectrometry of the analyte picked up by the swab and the analyte remaining on the substrate after swabbing. When analytical protocol was not amenable to a particular analyte or substrate a commercial explosive trace detection instrument was used. It was found that the substrate morphology played a bigger role in pickup of analyte than the particular analyte.

In order to eliminate biological warfare agents, both heat and halides are used. Ideally, these agents would be destroyed without dispersing them. The approach to create a polymeric-sprayable matrix would allow dispersion of an iodine-producing pyrotechnic, without dispersing the biological weapon, and when initiated would produce both heat and iodine gas. This matrix will provide iodine vapor and a long-lasting flame, not an explosion, to control dispersion of the threat.

A two-part foam was formulated based on polyurethane chemistry, i.e. a diisocyanate combined with polyol to produce a urethane linkage. Each component of the foam (e.g. isocyanate, polyol, catalyst, blowing agent, surfactant) was experimentally adjusted to achieve the best foam based on expansion, structural integrity, and cell uniformity. Since the polyol is the most adjustable component in the foam, an investigation of commercial and synthesized energetic polyols was performed. The structures of the energetic polyols were verified by LC-MS and FTIR and characterized for heat flow by DSC. Once the structures of the energetic polyols had been proven, it was formulated into a polyurethane foam which was characterized for heat of decomposition, by SDT, for heat of combustion by bomb calorimetry, and
structurally by FTIR. Documenting heat flow with SDT helped to determine that the structural modification increased heat release and lowered ignition temperature compared to the standard polyurethane foam. The formulated polyurethane foam was then tested for expansion against increased solids loading. When optimal solids loading was determined (>70%), the pyrotechnic foam was ignited in a bomb calorimeter. The heat released and iodine production was quantified.
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PREFACE

This thesis is prepared in the manuscript format. Chapter 1 is titled Electrostatically-enhanced swabbing for near field sampling; this work was funded by DHS. Chapter 2, Potential Biocides: Polymer Packaging of Iodine containing Pyrotechnics was funded by DTRA through grant HDTRA1-14-0027 and part of the manuscript is in preparation for publication. This document is written in Manuscript Format. Guidelines for formatting have been followed here and in the entirety of this document.
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Manuscript 1

Electrostatically Enhanced Swabbing for Near-Field Sampling

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ABSTRACT

Explosive detection often depends on collection of particles by swabbing potentially contaminated surfaces. We have found that the pickup of particles by commercials swabs can be improved by applying an electrostatic charge to the swab. Two methods of generating electrostatically charged swabs were tested--triboelectric versus corona discharge. They were compared examining charge magnitude, reproducibility, stability, and effects of humidity. The charge necessary for collection of particles was evaluated using an electrostatic voltmeter and measuring particle pickup. Enhancement of collection was judged by comparing pickup by electrostatically enhanced Nomex® swabs with that achieved by contact swabbing. The efficiency of contact versus non-contact electrostatic swabbing was tested against two variables—analyte (TNT, RDX, PETN, and ammonium nitrate) and 13 substrates. Mass spectrometry was used to quantify analyte pickup by mass balance of the analyte on the swab and remaining on the substrate. When quantification by mass spectrometry was impossible, electrostatic swabbing was evaluated and compared to contact with an explosive trace detector (i.e. ion mobility spectrometer).
INTRODUCTION

Effective explosive detection is of critical importance to law enforcement and government agencies. The Department of Homeland Security (DHS) has defined instruments which can pass certain tests, i.e. detecting specified explosives in a set amount of time, as explosive detection systems (EDS) or explosive trace detectors (ETD). A “trace explosive” is defined as not visible to the human eye, generally, material at the nanogram level [1-2]. Collecting trace amounts of explosive and transitioning them to a detector is the weak link in detection protocol. Much research in explosive detection is aimed at the development of selective and sensitive detectors, but these gains can be offset by inefficient analyte collection and introduction. Current swabs use materials, such as paper, Nomex, or Teflon, to mechanically scrape the analyte from a surface [3]. A dichotomy in explosive trace detection is that swabs must be effective at sorption as well as de-sorption, i.e. sorption to the surface and release into the detection device.

Generally, de-sorption is considered to be the more desirable property; therefore, polytetrafluoroethylene (PTFE) known as Teflon™ is one choice for commercial swabs [2]. Traditionally, swabbing is by direct contact. The contact swabbing of hands, headdresses, and medical appliances can increase the amount of contaminants on the swab and can be personally invasive. The ideal swabs would both enhanced sorption and de-sorption and require no contact with the subject or object.

This study considers application of electrostatic charge to commercial swabs. This can be accomplished three ways: triboelectric charging (friction), induction charging, or conduction. The classic conductive charging method uses a Van de Graaf
generator. The head of the Van de Graaf generator is negatively charged, and when a neutral object comes into contact with it, the charge is transferred [4]. This method was initially examined, but the charge was non-directional and short-lived on surfaces. Thus, only triboelectric and corona charging were further investigated.

When two materials with different electron affinities come in close proximity, the transfer of electrons creates separation of charge between the two surfaces [5-10]. The static charge created on the two surfaces can be positive or negative, depending on their relative position in the triboelectric series [7]. The triboelectric series lists materials in order of their preference to obtain a charge of relative magnitude in relationship to other materials (Figure 1.1).

The further away two materials exist on the triboelectric series, the higher the resulting magnitude of charge on the two materials. For example, PTFE is highly negative on the triboelectric series, and friction between it and a highly positive material in the series should result in two oppositely charged materials [5-6, 9]. This method of charging is termed “triboelectric charging.” This method might also result in transfer of contaminants. Inductively charging a swab can be achieved without
A corona needle (pinner) attached to a high voltage supply with low current ionizes the surrounding air molecules. When the pinner is in close proximity to a grounding plate, electrons migrate toward the grounding plate, passing through intervening surfaces, in this case, a swab. Thus, the swab is charged. The grounding plate may play a role in increasing the uniformity of charge (a concept investigated in this study). Inductive charging is used commercially, in one application to create a permanently polarized material, termed an electret. Electrets, like the Swiffer®, are formed by exposing a material to polarized electric fields at high temperature [11-14].

In theory, any material with a measurable relative permittivity should be subject to electrostatic enhancement [15-16]. In this work, the potential for non-contact electrostatic swabbing was investigated and benchmarked to performance of standard contact swabs.

**EXPERIMENTAL METHODS**

**Swabs & Substrates**

Teflon (PTFE) and Nomex swabs were supplied by FLIR Detection. PTFE-coated fiberglass and cotton swabs were supplied by DSA Detection and no modifications were made. Substrates were cut from bulk material to approximately 1/2 inch by 2 inch. Bytac® substrate, (fluoroethylene propylene with vinyl backing) was purchased from Saint-Gobain. Aluminum foil substrate (the dull side) was obtained from Berkley Jensen. PTFE and cotton substrates were obtained from pieces of FLIR and DSA Detection swabs, respectively. Vinyl, high density polyethylene (HDPE), and polycarbonate substrates were purchased from McMaster-Carr. (The latter two required a scroll saw to cut). Ballistic nylon was purchased online from Amazon. The
ABS (acrylonitrile butadiene styrene) substrate was printed into flat pieces on a MakerBot 3-D printer. The white Nylon 1000 substrate was purchased from Rockywoods (The white substrate was used because the solvent extracted the black dye). Zipper substrates were plastic pull tabs (polyurethane) purchased from Ohio Travel Bag. The cardboard substrate was created by pulling apart a cardboard corrugated sheet so that just the first layer was used. Polypropylene wrapping material, verified by FTIR using attenuated total reflectance (ATR) was also used.

**Scanning Electron Microscopy (SEM)**

Scanning electron micrographs were obtained at 20 kV in secondary ion mode on a JEOL 5900 SEM of some of the substrates and swabs. Secondary ion mode was used because it specifically focused on the surface morphology.

**Analytes**

Initially, commercial sugar and sodium chloride were used as surrogates for organic explosives and inorganic energetics, respectively. These were sieved to control particle size to approximately 800 microns. Organic explosives 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1 3 5-triazacyclohexane (RDX), Pentaerythritol tetranitrate (PETN), C-4, and an inorganic energetic material ammonium nitrate (AN) were obtained from military or industrial sources (Figure 1.2).

![Chemical structures of PETN, TNT, RDX](image)

**Figure 1.2. Chemical structures of PETN, TNT, RDX**
**Humidity Measurements**

A humidity chamber was built using a humidistat and glove box. Controlled humidity environments were achieved with saturated salt solutions [17]. Experiments at 0% humidity used dry compressed air.

**Dry Transfer**

Trace quantities of solid analyte were placed on surfaces as solutions of known concentrations via micro-syringe and solvent allowed to evaporate. This resulted in an unrealistic distribution of analyte on the surface (e.g. coffee rings); therefore, a dry transfer method was developed [18]. The solution of analyte was placed by Eppendorf pipette (2-20 μL) onto a strip of Bytac®. The solvent was allowed to evaporate from the Bytac, and the resulting residue on the Bytac® was transferred to the desired substrate by rubbing the Bytac over the substrate in one direction.

**Preparation of Analytes**

Analytical standards were made by starting with a 1 mg/mL solution of the analyte and performing subsequent serial dilution in appropriate solvents. For organic explosives, the solvent was either HPLC grade acetone or 50:50 HPLC grade acetonitrile: Optima® water. For inorganic explosives the solvent was ultra-pure 18 MΩ water. Each test series began by directly spiking 500 ng of analyte onto Bytac. Subsequent analysis of the amount of analyte remaining on the Bytac, the substrate, or the swab was performed as follows. For the organic analytes, the substrates were put in 15 mL polypropylene conical vials with 7-10 mL of HPLC grade methanol. In addition, each substrate without analyte went through the same extraction conditions as controls. Vials were shaken for ~1 min, vortexed for ~1 min, sonicated for 15 min,
vortexed ~ 1 min, and transferred to clean glass conical vials. Vials were evaporated to
dryness using an Organomation Nitrogen evaporation system with compressed air and
a water bath at 40°C. Solutions were reconstituted with the appropriate amount of
50:50 acetonitrile: water to achieve a final concentration of 500 ng/mL. The solution
(400 µL) was transferred into a LC vial, syringe filtered through a PTFE 0.22 µm
filter, and 20 µL of a 5000 µg/mL solution of 2,4-dichlorophenoxyacetic acid was
added to each vial as an internal standard.

**Quantification of Organic Analytes**

For organic analytes, quantification was accomplished by an Accela 1250
liquid chromatograph with Thermo Scientific TSQ Quantiva triple quadrupole mass
spectrometer (LC/MS). A heated electrospray ionization (HESI) source created ions
that went to an ion transfer tube at 300°C. Conditions used in HESI analysis Table 1.1.

| Conditions for HESI source | Value |
|----------------------------|-------|
| negative ion spray voltage (V) | 2500 |
| sheath gas (AU) | 40 |
| auxiliary gas (AU) | 12 |
| sweep gas (AU) | 1 |
| vaporizer temperature (°C) | 260 |

Sample injections of 20 µL were by a CTC Analytics HTS PAL auto sampler
from glass LC sample vials with PTFE septa. The 20 µl aliquot was at a flow rate of
300 µL/min with initial conditions of 95 % aqueous 200 µM ammonium chloride, 200
µM ammonium acetate, 1% formic acid and 5% methanol, then at 5 min the
conditions changed to 5% aqueous 200 µM ammonium chloride, 200 µM ammonium
acetate, 1% formic acid and 95% methanol. At 7 minutes the solvent ratio returned to
the initial conditions and held until the completion of injection cycle at 8 minutes. The
LC column was a Thermo Scientific Acclaim Polar Advantage II C18 (PA2, 2.1x50 mm, 3 μm, 120 Å). Multiple reaction monitoring (MRM) transitions are shown for each compound in Table 1.2.

Table 1.2. MRM transitions for organic explosive analytes

| Compound   | Precursor (m/z) | Product (m/z) | Collision Energy (V) | Retention Time (min) |
|------------|----------------|---------------|----------------------|----------------------|
| PETN       | 351.03         | 46.15         | 16.93                | 5.6                  |
|            | 351.03         | 62.11         | 10.25                |                      |
| TNT        | 226.03         | 46.24         | 26.58                | 5.0                  |
|            | 226.03         | 165.93        | 15.31                |                      |
|            | 226.03         | 196.09        | 12.83                |                      |
| RDX        | 257.12         | 35.24         | 32.50                | 4.8                  |
|            | 257.12         | 46.01         | 28.35                |                      |
|            | 257.12         | 82.17         | 10.25                |                      |
| 2,4-Dichlorophenoxyacetic acid | 219.00 | 89.04 | 34.88 | 6.4 |
|            | 219.00         | 125.00        | 27.04                |                      |
|            | 219.00         | 160.94        | 13.03                |                      |

Curves were analyzed and linearly correlated between the ratio of internal standard and the analyte which was weighted (1/x²) by Thermo Xcalibur Quan Browser software version 3.0.63. An example of a standard curve can be seen in Figure 1.3. Dynamic range for PETN analysis was from 10 to 2500 ng/mL; for TNT, 25 to 5000 ng/mL; and for RDX, from 10 to 2500 ng/mL.

![Figure 1.3. Example of a calibration curve for PETN](image-url)
Explosive Trace Detectors (ETD)

The commercial ETD used in these experiments was a Morpho Itemiser DX ion mobility spectrometer (IMS). The compatible swab for this instrument was PTFE-coated fiberglass. The sensitivity of the ETD was evaluated by dosing swabs directly with 10-250 nanograms of PETN or 100-10,000 nanograms AN. For PETN 100 ng of analyte was deposited from a solution of acetone onto Bytac® and allowed to dry. For AN 500 ng of analyte was deposited from a solution of water onto Bytac and allowed to dry. For both analytes, the dry transfer method was employed from Bytac® to various substrates (Figure 1.4). For contact swabs, the swab physically contacted the substrate with ~7 N of force. Electrostatic swabs were charged at -20 kV, 2 inches from the swab for 5 seconds. Voltages were recorded with a 3M 718 electrostatic voltmeter, and passed along the substrate from a distance of ~10 mm. In each test, after swabbing the substrate, the swab was placed in the heated inlet of the IMS. If an IMS response of “NO ALARM” occurred, the swab was recharged and the substrate re-swabbed; this attempt to get an alarm was repeated up to three times.

Figure 1.4. Setup for the dry transfer of analyte to each substrate
RESULTS AND DISCUSSION

**Bulk Measurements**

As a proof of concept, electrostatic pick up of visible amounts of surrogate analytes, sucrose and sodium chloride, was performed (Figure 1.5, Table 1.3). An electrostatic charge was applied to PTFE swabs by rubbing the swab on a polyurethane foam roller. This triboelectric charging method resulted in swabs with charges ranging from -1.32 kV to -3.61 kV. For the sucrose and sodium chloride data, the relative humidity (RH) was 41% and 24%, respectively. On an index card, 100 milligrams of analyte was placed, and the charged swab was held over it at a fixed distance—0, 10, 20, 30, 50, and 100 millimeters. For comparison, an uncharged swab, was tested in a similar fashion. Efficiency of pickup was judged by the amount of analyte remaining on the index card. Each test was done in triplicate. The nature of the analyte, organic versus ionic, did not appear to affect the extent of pickup. However, as expected, the farther away the swab was from the analyte, the less efficient the pickup. There was a significant drop off from 20 mm to 30 mm. Results suggest the maximum effective distance for any analyte transfer to a triboelectrically charged swab is likely to be ~50 mm. Without a charge no significant amount of mass was picked up at a distance greater than 0 millimeters. (Table 1.4).
To determine the minimum charge necessary for pickup of analyte, 30 mg of either PETN or AN were placed on an index card, and a PTFE swab was triboelectrically charged, to voltages ranging 0.1 kV - 1 kV. From a height of 10 mm, analyte pickup was attempted. Both the index card and swab were weighed on an analytical balance. Both analytes were picked up, even at these low voltages, although, the highest pickup was (5 mg) which amounts to ~15% recovery (Figure 1.6).
Table 1.3. Bulk Measurements of mass pickup of sucrose & NaCl on charged swabs

| Distance (mm) | Mass sucrose adsorbed (mg) | Charge (-kV) | Average sucrose adsorbed (mg) | Std Dev (mg) | Distance (mm) | Mass NaCl adsorbed (mg) | Charge (-kV) | Average NaCl adsorbed (mg) | Std Dev (mg) |
|--------------|---------------------------|-------------|--------------------------------|--------------|--------------|------------------------|-------------|----------------------------|--------------|
| 0            | 39.8                      | 2.85        |                                |              | 0            | 41.1                   | 2.31        |                            |              |
| 0            | 38.5                      | 3.14        |                                |              | 0            | 42.5                   | 2.64        |                            |              |
| 0            | 35.0                      | 2.47        |                                |              | 0            | 44.5                   | 3.18        |                            |              |
| 10           | 27.3                      | 2.85        |                                |              | 10           | 51.4                   | 3.61        |                            |              |
| 10           | 21.6                      | 2.41        |                                |              | 10           | 32.3                   | 1.81        |                            |              |
| 10           | 28.6                      | 3.34        |                                |              | 10           | 29.0                   | 2.67        |                            |              |
| 20           | 14.9                      | 2.17        |                                |              | 20           | 17.6                   | 2.25        |                            |              |
| 20           | 17.4                      | 2.85        |                                |              | 20           | 22.5                   | 2.52        |                            |              |
| 20           | 16.8                      | 1.32        |                                |              | 20           | 16.1                   | 2.01        |                            |              |
| 30           | 3.5                       | 2.75        |                                |              | 30           | 9.4                    | 3.47        |                            |              |
| 30           | 3.6                       | 2.35        |                                |              | 30           | 4.6                    | 2.64        |                            |              |
| 30           | 5                         | 2.91        |                                |              | 30           | 6.8                    | 2.83        |                            |              |
| 50           | 3                         | 2.34        |                                |              | 50           | 2.5                    | 3.00        |                            |              |
| 50           | 5                         | 2.72        |                                |              | 50           | 2                      | 3.59        |                            |              |
| 50           | 2                         | 1.89        |                                |              | 50           | 0                      | 2.73        |                            |              |
| 100          | 0                         | 3.12        |                                |              | 100          | 0                      | 2.25        |                            |              |
| 100          | 0                         | 2.46        |                                |              | 100          | 1                      | 3.28        |                            |              |
| 100          | 0                         | 2.38        |                                |              | 100          | 0                      | 3.50        |                            |              |

Table 1.4. Bulk measurements pickup of sucrose and NaCl on uncharged swabs

| Distance (mm) | Mass sucrose adsorbed (mg) | Charge (kV) | Distance (mm) | Mass NaCl adsorbed (mg) | Charge (kV) |
|--------------|---------------------------|-------------|--------------|------------------------|-------------|
| 0            | 1.5                       | 0.02        | 0            | 1.9                    | 0.03        |
| 0            | 1.1                       | 0.08        | 0            | 2.8                    | 0.02        |
| 0            | 0.5                       | 0           | 0            | 3.1                    | 0.05        |
| 10           | 0                         | 0.03        | 10           | 0                      | 0.04        |
| 10           | 0                         | 0.08        | 10           | 0.2                    | 0.07        |
| 10           | 0.4                       | 0.05        | 10           | 0.3                    | 0.01        |
**SEM Micrographs**

Figure 1.7. SEM micrographs of select substrates (top rows) and swabs (bottom row)

**Method for charging swabs**

To charge swabs inductively, a pinner was fixed over an unheated hot plate base which had been covered with a perforated metal (zinc coated steel) grounding plate (Figure 1.8). The grounding plate had a screw in one corner and a wire which was fixed to the screw of a traditional electrical outlet (A schematic is shown in Figure 1.9). The contact was tested with a multi-meter to verify proper grounding. Since the use of inductive charging relies on the attraction of a charge through the swab to a base, various bases were examined (Table 1.5). Tests were performed charging at -20 kV and 2 inches from the swab for 5 seconds at 40% RH. Voltages were measured using a 3M 718 electrostatic voltmeter, and a static dissipater was used to eliminate excess charge before each experiment. Results, shown in Table 1.5, indicated no change in the base surface would be necessary.
Figure 1.8. Hot plate with grounding wire and the grounding connection at outlet

Figure 1.9. Schematic of the inductive charger

Table 1.5. Potential Surface for Charging Station tested with PTFE and Nomex swabs

| Nomex swab, base (thickness in) | Initial Charge (kV) | wait time 30 sec (kV) | wait time 60 sec (kV) | Teflon swab, base (thickness in) | Initial Charge (kV) | wait time 30 sec (kV) | wait time 60 sec (kV) |
|--------------------------------|---------------------|----------------------|----------------------|--------------------------------|---------------------|----------------------|----------------------|
| Hotplate 1.504                 | -11.98              | -12.21               | -12.31               | Hotplate 1.504                 | -9.34               | -6.34                | -5.17                |
| 2                              | -13.03              | -13.87               | -12.21               | 2                              | -8.53               | -6.22                | -5.03                |
| 3                              | -13.04              | -13.42               | -11.98               | 3                              | -7.53               | -5.40                | -4.98                |
| ABS 0.132                      | -1.12               | -1.22                | -1.13                | ABS 0.132                      | -0.64               | -0.57                | -0.57                |
| 2                              | -0.97               | -0.97                | -0.97                | 2                              | -1.51               | -1.49                | -1.39                |
| 3                              | -2.12               | -1.90                | -1.87                | 3                              | -1.25               | -1.24                | -1.26                |
| Acrylic 0.16                   | -7.47               | -6.76                | -6.93                | Acrylic 0.16                   | -2.68               | -2.55                | -2.42                |
| 2                              | -10.28              | -10.86               | -9.68                | 2                              | -2.46               | -2.49                | -2.63                |
| 3                              | -6.03               | -6.33                | -5.57                | 3                              | -1.29               | -1.27                | -1.24                |
| Wood 0.41                      | -5.26               | -5.36                | -5.34                | Wood 0.41                      | -3.51               | -3.15                | -3.02                |
| 2                              | -5.62               | -5.46                | -5.51                | 2                              | -2.90               | -3.12                | -2.99                |
| 3                              | -9.36               | -8.27                | -7.36                | 3                              | -3.64               | -3.14                | -3.13                |
| Polymer Resin 0.90             | +0.66               | +0.54                | +0.64                | Polymer Resin 0.90             | +0.58               | +0.48                | +0.48                |
| 2                              | +0.49               | +0.41                | +0.45                | 2                              | +0.18               | +0.31                | +0.31                |
| 3                              | +0.21               | +0.22                | +0.18                | 3                              | +0.48               | +0.48                | +0.47                |
| Metal 0.05                     | -12.53              | -10.30               | -8.56                | Metal 0.05                     | -3.50               | -3.29                | -3.08                |
| 2                              | -8.94               | -7.86                | -7.60                | 2                              | -3.20               | -3.10                | -3.11                |
| 3                              | -10.54              | -9.91                | -8.33                | 3                              | -2.92               | -2.80                | -2.79                |
| Ceramic 0.50                   | -0.42               | -0.38                | -0.32                | Ceramic 0.50                   | -0.26               | -0.21                | -0.10                |
| 2                              | -0.88               | -0.83                | -0.75                | 2                              | -0.30               | -0.10                | -0.12                |
| 3                              | -0.57               | -0.54                | -0.58                | 3                              | -0.25               | -0.18                | -0.09                |
**Humidity Measurements**

Humidity affects the generation of electrostatic charges both on the molecular and macroscopic level [19]. In electrostatic precipitators, it has been shown that collection efficiency of small particles (<50 μm) increases with increasing humidity, and that negative corona discharge is less sensitive to humidity than positive [20]. The effects of humidity were examined on three swabs. They were held in air over a 3-min time period (Figures 1.10, 1.11, 1.12). In the 0% RH-30% RH regime there was little change in the initial magnitude; the decay was less than 1 kV; however, in the 50% RH and 80% RH regime, a significant drop in initial magnitude was observed. This was consistent with literature reports that at low levels of humidity, the charges are inserted directly into the bulk volume, whereas if moisture can accumulate on the surface of the material, the charge decays slowly into the bulk [21].
Figure 1.10. PTFE-coated fiberglass swab effective voltage with increasing humidity

Figure 1.11. FLIR Nomex swab effective voltage with increasing humidity

Figure 1.12. FLIR PTFE swab effective voltage with increasing humidity
With cotton swabs, it was difficult to achieve and maintain a negative charge. This we attribute to the position of cotton on the triboelectric series (Figure 1.2). Three cotton swabs were charged at 30% RH and held in air over a three-minute period. The charge on the swab grew more positive with time (Figure 1.13).

![Figure 1.13](image.png)

Figure 1.13. DSA Cotton swab held at 30%RH positively charged over 3 minutes

In addition to observing charge retention on the swab with various RH, pickup efficiency was also examined using sucrose and ground glass. Humidity had little effect on the pickup of the ground glass by the PTFE swabs; but sucrose pickup was greater at high RH than at low, contrary to our expectations (Figure 1.14). While high RH reduced charge accumulation on the swab (Figures 1.9, 1.10, 1.11), the increased pickup of sucrose may be related to its solubility in water.

![Figure 1.14](image.png)

Figure 1.14. Mass pickup of sucrose & ground glass at increasing humidity a voltage
Swabbing and Swab Preparation

For contact swabs, they were physically rubbed against the substrate with the experimenter attempting to apply ~7 N of force [22-23]. Electrostatically enhanced swabs were charged by the inductive charging method and then passed along the substrate from a distance of ~10 mm.

Charging and storage of swabs in stacked and unstacked configuration

Commercially purchased swabs are packaged in multi-swab packages. In order to determine if swabs could be packaged charged or if charging of multiple swabs could occur concurrently, studies were performed examining mass charging and storage of swabs. Attempts to charge (-20 kV for 5 seconds) in a stacked configuration, resulted in only the top swab, i.e. about 2 inches from the pinner, being charged, negatively; the entire 10-swab stack was not charged. This was true for 5-swab, 4-swab and 3-swab stacks. In a 2-swab stack both swabs were charged. For one set of measurements (Table 1.6 -left), the 2-swab stack was picked up together and pulled apart prior to measurement of the charge. This left the top swab charged negatively and the bottom swab charged positively. In a second test, (Table 1.6-right), the 2-swab stack was separated while the bottom swab remained in contact with the aluminum foil; however, charge measurement on both the top and bottom swabs were performed as the swab was held in air. The results suggest that transfer of charge can occur during swab separation.

Table 1.6. Two-swab stack charged together & separated after lifting together in air (left) or separated with one remained in surface contact (right) (experiment performed in triplicate)

| top (kV) | -11.05 | -11.97 | -17.55 |
|---------|--------|--------|--------|
| bottom (kV) | 4.96 | 4.98 | 9.84 |
| top (kV) | -7.85 | -8.41 | -9.44 |
| bottom (kV) | -6.43 | -6.54 | -5.21 |
In another experiment, tests were performed (trial 1 at 40% RH and Trial 2 at 30% RH) in which 10 Nomex or 10 PTFE swabs were charged simultaneously at -20 kV for 5 seconds in an unstacked configuration as shown in Figure 1.15. They were stored individually or in stacks of 10 or 5 for 24 hours on aluminum foil. The initial position of the swabs (Figure 1.15) did not have a significant effect on initial charge of the swabs. The Nomex had a higher charge than the PTFE (Tables 1.7 and 1.8).

![Figure 1.15. Arrangement of swabs charged simultaneously from 2 inches height](image)

A trial of 10 swabs were placed, individually, 24 hours at 22°C; and another trial of 10 were stored stacked on aluminum foil. For swabs left unstacked, the voltage decay was negligible during that 24-hour period; for swabs stored in a stack, the change in charge varied wildly. Acknowledging that like charges repel, over 24 hours, the charges on Nomex migrated through the swab stack to create a large charge separation. However, for the PTFE stack, the bottom and top swabs are positively charged with the largest absolute difference in charge. In the replicate experiments, there was still much variation in charge created and retained. After 24 hours of storage, in all cases, the top swab of a 10-swab stack had experienced the most change in charge and was more positively charged than the bottom swab. When the storage stack size was reduced from 10 swabs to five, the same trends were observed as with
the 10-swab stack, i.e. the top swab experienced the largest change in charge and was the most positively charged of the stack after 24 hours Table 1.9.

Table 1.7. Nomex swab charged inductively & stored stacked on Al foil for 24 hr

| Trial 1 | Trial 2 |
|---------|---------|
| swab    | initial charge (kV) | charge at 24 hours (kV) | absolute difference |
|---------|---------------------|------------------------|---------------------|
| bottom -> | 1     | -10.71           | -12.49            | 1.78               |
|         | 2     | -6.57            | -2.46             | 4.11               |
|         | 3     | -11.48           | -5.69             | 5.79               |
|         | 4     | -10.3            | -5.72             | 4.58               |
|         | 5     | -11.41           | 2.03              | 13.44              |
|         | 6     | -7.87            | -2.82             | 5.05               |
|         | 7     | -11.69           | 5.25              | 16.94              |
|         | 8     | -11.66           | -5.95             | 5.71               |
|         | 9     | -11.2            | -2.32             | 8.88               |
| top ->  | 10    | -10.85           | 7.06              | 17.91              |

Table 1.8. PTFE swab charged inductively & stored stacked on Al foil for 24 hr

| Trial 1 | Trial 2 |
|---------|---------|
| swab    | initial charge (kV) | charge at 24 hours (kV) | absolute difference |
|---------|---------------------|------------------------|---------------------|
| bottom -> | 1     | -2.21             | 5.48                 | 7.69                |
|         | 2     | -5.32             | -3.99                | 1.33                |
|         | 3     | -4.99             | -1.73                | 3.26                |
|         | 4     | -4.37             | 1.03                 | 5.4                 |
|         | 5     | -3.68             | -2.1                 | 1.58                |
|         | 6     | -3.58             | -1.51                | 2.07                |
|         | 7     | -5.05             | -3.54                | 1.51                |
|         | 8     | -5.52             | -1                   | 4.52                |
|         | 9     | -4.89             | -3.87                | 1.02                |
| top ->  | 10    | -3.83             | 9.37                 | 13.2                |

Table 1.9. Nomex swabs inductively charged & stored stack on Al foil for 24 hr

| Bottom | initial charge (kV) | charge at 24 hours (kV) |
|--------|---------------------|------------------------|
| -13.02 | 3.41                | -11.14                 | 4.02                | -12.22 | 5.39 |
| -13.14 | -1.96               | -12.25                 | -5.19               | -11.43 | -12.32 |
| -12.92 | -3.52               | -10.49                 | -7.86               | -12.69 | -8.97 |
| -11.62 | -4.37               | -9.65                  | 2.51                | -13.22 | -3.94 |

| Top    | initial charge (kV) | charge at 24 hours (kV) |
|--------|---------------------|------------------------|
| -13.86 | 10.95               | -10.93                 | 6.57                | -10.46 | 9.11 |
Quantification of Analytes

The remainder of this study examined pickup efficiency of electrostatic swabs compared to contact swabs. Substrates examined are shown in (Figure 1.16).

| Material                  |
|---------------------------|
| Al Foil (metal)           |
| PTFE                      |
| Vinyl                     |
| ABS                       |
| Cotton                    |
| Polycarbonate (PC)        |
| High Density Polyethylene (HDPE) |
| Nylon 1000                |
| Ballistic Nylon           |
| Ohio Zipper               |
| Cardboard                 |
| Packing Tape              |
| Bytac®                    |

Figure 1.16. Substrates used in this study

The experiment to examine pickup from each substrate was conducted in three parts. First, to determine the extraction efficiency from each substrate, three substrates were directly spiked with 500 ng of analyte in solvent; the solvent was allowed to evaporate; the substrates were extracted with another solvent; the solvent was adjusted to proper volume; and a portion was analyzed by LC/MS. The result indicated the amount of the original 500 ng of explosive that could be recovered from the surface of a given substrate. An example of this using polycarbonate (PC) as substrate S1 is shown in top 3 lines Table 1.10.

Then six samples of Bytac® were spiked with 500 ng of the analyte and rubbed against substrate the first substrate S2 and both S1 and S2 were analyzed to the dry transfer efficiency for a given substrate (middle section of Table 1.10). Three of these S2 and the three S1 against which they were rubbed (dry transferred) and were
extracted with solvent; the solvent was adjusted to proper volume, and was analyzed by LC/MS. The result indicated the amount of explosive that could possibly be transferred from S2 to the swab. That amount plus that remaining on S1 ideally would add to 500 ng (1, middle section). Then, six more Bytac® (S1) were directly spiked with 500 ng of analyte, dry transferred to S2, then three of the S2 were swabbed by contact, i.e. directly rubbing the Nomex swab against S2 (~7 N force) and three of the S2 were swabbed using the electrostatically enhanced Nomex swabs.

Then, these six swabs, S2, and S1 were extracted with solvent; the solvent was adjusted to proper volume; and a portion was analyzed by LC/MS. For any given set, the amount of explosive left on S1 and S2 and found on the swab should have added to 500 ng. The amount of explosive found on the three electrostatically enhanced swabs versus the three contact swabs is shown in Table 1.10 (bottom section) along with percent recovery. A metric of success is labeled Percent Recovery where the nanograms of analyte on the swab (contact or electrostatic) are divided by the total amount of nanograms recovered from 500 ng and displayed as a percentage. For example, in the last line of Table 1.10, 351 ng were found on the swab out of a total recovery of 475 ng. This translates to a 74% recovery.
**Polycarbonate**

The results shown in Table 1.10 for both contact and electrostatic swabs are below 100 ng, except for one outlier (3rd electrostatic swab). These results suggest analyte on polycarbonate is difficult to sorb onto a swab, whether contact or electrostatic. This could be related to the smoothness of the polycarbonate surface.

Table 1.10. Nomex contact & electrostatic swabbing for PETN from polycarbonate Electrostatic swabs charged to -8.99 kV, -10.23 kV, & -13.01 kV at RH 25%.

PETN was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng PETN out of 500ng |
|----------------------------------|--------------------------------------|---------------------|
| Polycarbonate                    | --                                   | 424                 |
| Polycarbonate                    | --                                   | 413                 |
| Polycarbonate                    | --                                   | 328                 |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng PETN recovered from 500 ng |
|----------------------------------|--------------------------------------|----------------|----------------|-----------------------------------|
| Bytac                            | Polycarbonate                        | 228            | 267            | 495                               |
| Bytac                            | Polycarbonate                        | 312            | 136            | 448                               |
| Bytac                            | Polycarbonate                        | 13             | 372            | 385                               |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng PETN on Nomex by CONTACT swabbing | ng PETN on Nomex by ELECTROSTATIC swabbing | Total ng PETN recovered from 500 ng | Percent Recovery % |
|----------------------------------|--------------------------------------|----------------|----------------|------------------------------------|--------------------------------------------|-----------------------------------|-------------------|
| Bytac                            | Polycarbonate                        | 326            | 160            | 95                                 | 581                                        | 16                                |                   |
| Bytac                            | Polycarbonate                        | 114            | 281            | 44                                 | 439                                        | 10                                |                   |
| Bytac                            | Polycarbonate                        | 99             | 212            | 41                                 | 352                                        | 12                                |                   |
| Bytac                            | Polycarbonate                        | 228            | 155            | 92                                 | 475                                        | 19                                |                   |
| Bytac                            | Polycarbonate                        | 74             | 269            | 86                                 | 429                                        | 20                                |                   |
| Bytac                            | Polycarbonate                        | 13             | 111            | 351                                | 475                                        | 74                                |                   |
The electrostatic swabs outperformed contact with an average pickup efficiency of 39% versus 13% for contact (Table 1.11).

Table 1.11. Nomex contact and electrostatic swabbing for PETN from cardboard

Electrostatic swabs charged to -7.32 kV, -9.65 kV, & -9.89 kV at RH 30%.

PETN was deposited from a solution of acetone.
Bytac®

The average total recovery was low but the electrostatically enhanced swab recovered more PETN than the contact swabs (Table 1.12).

Table 1.12. Nomex contact and electrostatic swabbing for PETN from Bytac®

Electrostatic swabs charged to -8.17 kV, -9.37 kV & -10.28 kV at RH 5%.

PETN was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng PETN out of 500ng |
|----------------------------------|--------------------------------------|----------------------|
| Bytac                            | --                                   | 486                  |
| Bytac                            | --                                   | 526                  |
| Bytac                            | --                                   | 483                  |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng PETN recovered from 500 ng |
|----------------------------------|--------------------------------------|----------------|----------------|-------------------------------------|
| Bytac                            | Bytac                                | 408            | 26             | 434                                 |
| Bytac                            | Bytac                                | 311            | 244            | 555                                 |
| Bytac                            | Bytac                                | 279            | 261            | 540                                 |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng PETN on Nomex by CONTACT swabbing | ng PETN on Nomex by ELECTROSTATIC swabbing | Total ng PETN recovered from 500 ng | Percent Recovery % |
|----------------------------------|--------------------------------------|----------------|----------------|--------------------------------------|-------------------------------------------|-----------------------------------|-------------------|
| Bytac                            | Bytac                                | 439            | 22             | 7                                    | 468                                       | 2                                 | 2.0               |
| Bytac                            | Bytac                                | 291            | 44             | 15                                   | 350                                       | 4                                 | 4.0               |
| Bytac                            | Bytac                                | 360            | 52             | 10                                   | 421                                       | 2                                 | 2.0               |
| Bytac                            | Bytac                                | 383            | 62             | 20                                   | 465                                       | 4                                 | 4.0               |
| Bytac                            | Bytac                                | 123            | 212            | 108                                  | 444                                       | 24                                | 24.0              |
| Bytac                            | Bytac                                | 168            | 50             | 123                                  | 340                                       | 36                                | 36.0              |
**Acrylonitrile Butadiene Styrene (ABS)**

ABS is a common material for hard-sided baggage. Electrostatically enhanced swabs picked up more PETN than contact swabs Table 1.13.

Table 1.13. Nomex contact and electrostatic swabbing for PETN from ABS. Electrostatic swabs charged to -7.89 kV, -9.21 kV, & -10.24 kV at RH 35%. PETN was deposited from a solution of isopropanol.

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | Pretreatment of Substrate (S1) for direct deposit | Pretreatment of Substrate (S2) onto which dry transfer | ng PETN out of 500ng | Total ng PETN recovered from 500 ng |
|----------------------------------|--------------------------------------|-----------------------------------------------|------------------------------------------------|-----------------|----------------------------------|
| ABS                              | --                                   | ELECTROSTATIC swabbing                         | CONTACT swabbing                                | 424             |                                  |
| ABS                              | --                                   | ELECTROSTATIC swabbing                         | CONTACT swabbing                                | 362             |                                  |
| ABS                              | --                                   | ELECTROSTATIC swabbing                         | CONTACT swabbing                                | 450             |                                  |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | Pretreatment of Substrate (S1) for direct deposit | Pretreatment of Substrate (S2) onto which dry transfer | Total ng PETN recovered from 500 ng |
|----------------------------------|--------------------------------------|-----------------------------------------------|------------------------------------------------|----------------------------------|
| Bytac                            | ABS                                  | CONTACT swabbing                              | ELECTROSTATIC swabbing                          | 546               |
| Bytac                            | ABS                                  | CONTACT swabbing                              | ELECTROSTATIC swabbing                          | 531               |
| Bytac                            | ABS                                  | CONTACT swabbing                              | ELECTROSTATIC swabbing                          | 429               |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | Pretreatment of Substrate (S1) for direct deposit | Pretreatment of Substrate (S2) onto which dry transfer | ng PETN on Nomex by ELECTROSTATIC swabbing | ng PETN on Nomex by CONTACT swabbing | Total ng PETN recovered from 500 ng | Percent Recovery % |
|----------------------------------|--------------------------------------|-----------------------------------------------|------------------------------------------------|----------------------------------|----------------------------------|----------------------------------|-------------------|
| Bytac                            | ABS                                  | CONTACT swabbing                              | ELECTROSTATIC swabbing                          | 104                | 456                | 23                             |
| Bytac                            | ABS                                  | CONTACT swabbing                              | ELECTROSTATIC swabbing                          | 70                 | 464                | 15                             |
| Bytac                            | ABS                                  | CONTACT swabbing                              | ELECTROSTATIC swabbing                          | 154                | 438                | 35                             |
| Bytac                            | ABS                                  | CONTACT swabbing                              | ELECTROSTATIC swabbing                          | 158                | 526                | 30                             |
| Bytac                            | ABS                                  | CONTACT swabbing                              | ELECTROSTATIC swabbing                          | 208                | 524                | 40                             |
| Bytac                            | ABS                                  | CONTACT swabbing                              | ELECTROSTATIC swabbing                          | 315                | 459                | 69                             |
PTFE

Using PTFE as a substrate, electrostatic-enhanced non-contact swabs exhibited better pickup than the contact swab (Table 1.14). PTFE is known for its ‘non-stick’ properties. This property is so effective that some of the solvent deposited PETN slipped off the substrate, which explained often poor recovery. The recovery was much better for TNT, Table 1.15. The electrostatically enhanced swabs outperformed contact swabbing. TNT is less crystalline than PETN and tends to adhere to surfaces more effectively than PETN.

Table 1.14. Nomex contact and electrostatic swabbing for PETN from PTFE

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng PETN out of 500ng |
|----------------------------------|---------------------------------------|---------------------|
| PTFE                             | --                                   | 7                   |
| PTFE                             | --                                   | 251                 |
| PTFE                             | --                                   | 186                 |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng PETN recovered from 500ng |
|----------------------------------|---------------------------------------|----------------|----------------|----------------------------------|
| Bytac                            | PTFE                                 | 322            | 94             | 416                             |
| Bytac                            | PTFE                                 | 334            | 150            | 484                             |
| Bytac                            | PTFE                                 | 366            | 157            | 523                             |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng PETN on Nomex by ELECTROSTATIC swabbing | ng PETN on Nomex by CONTACT swabbing | Total ng PETN recovered from 500ng | Percent Recovery % |
|----------------------------------|---------------------------------------|----------------|----------------|------------------------------------------|------------------------------------|-------------------------------|---------------------|
| Bytac                            | PTFE                                 | 326            | 2              | 50                                       | 378                                 | 378                           | 13                  |
| Bytac                            | PTFE                                 | 93             | 9              | 90                                       | 192                                 | 192                           | 47                  |
| Bytac                            | PTFE                                 | 183            | 2              | 43                                       | 228                                 | 228                           | 19                  |
| Bytac                            | PTFE                                 | 357            | 2              | 57                                       | 417                                 | 417                           | 14                  |
| Bytac                            | PTFE                                 | 381            | 1              | 100                                      | 482                                 | 482                           | 21                  |
| Bytac                            | PTFE                                 | 58             | 21             | 140                                      | 219                                 | 219                           | 64                  |
Table 1.15. Nomex contact and electrostatic swabbing for TNT from PTFE
Electrostatic swabs charged to -7.41 kV, -10.28 kV, & -8.56 kV at RH 30%.
TNT was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng TNT out of 500ng |
|-----------------------------------|--------------------------------------|---------------------|
| PTFE                              | --                                   | 467                 |
| PTFE                              | --                                   | 427                 |
| PTFE                              | --                                   | 423                 |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng TNT recovered from 500ng |
|-----------------------------------|--------------------------------------|-----------------|-----------------|----------------------------------|
| Bytac                             | PTFE                                 | 140             | 254             | 393                              |
| Bytac                             | PTFE                                 | 122             | 278             | 400                              |
| Bytac                             | PTFE                                 | 144             | 300             | 444                              |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng TNT on Nomex by CONTACT swabbing | ng TNT on Nomex by ELECTROSTATIC swabbing | Total ng TNT recovered from 500ng | Percent Recovery % |
|-----------------------------------|--------------------------------------|-----------------|-----------------|-------------------------------------|-------------------------------------------|---------------------------------|-------------------|
| Bytac                             | PTFE                                 | 114             | 274             | 66                                  | 454                                       | 15                              |                    |
| Bytac                             | PTFE                                 | 104             | 247             | 44                                  | 395                                       | 11                              |                    |
| Bytac                             | PTFE                                 | 175             | 199             | 31                                  | 405                                       | 8                               |                    |
| Bytac                             | PTFE                                 | 59              | 292             | 41                                  | 392                                       | 10                              |                    |
| Bytac                             | PTFE                                 | 98              | 174             | 118                                 | 390                                       | 30                              |                    |
| Bytac                             | PTFE                                 | 92              | 227             | 82                                  | 401                                       | 20                              |                    |
**High Density Polyethylene (HDPE)**

HDPE, a very smooth plastic; thus, Bytac® did not efficiently transfer the analyte to it. Data in Table 1.16 indicates that the electrostatic swabs slightly outperformed the contact swabs. In the TNT study, Table 1.17, results were similar.

Table 1.16. Nomex contact and electrostatic swabbing for PETN from HDPE. Electrostatic swabs charged to -10.23 kV, -8.41 kV, & -8.55 kV at RH 40%. PETN was deposited from a solution of acetone.

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng PETN out of 500ng | Total ng PETN recovered from 500 ng |
|-----------------------------------|----------------------------------------|---------------------|-----------------------------------|
| HDPE                              | --                                     | 418                 |                                   |
| HDPE                              | --                                     | 456                 |                                   |
| HDPE                              | --                                     | 426                 |                                   |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng PETN on Nomex by CONTACT swabbing | ng PETN on Nomex by ELECTROSTATIC swabbing | Total ng PETN recovered from 500 ng | Percent Recovery % |
|-----------------------------------|----------------------------------------|-----------------|----------------|--------------------------------------|------------------------------------------|----------------------------------|---------------------|
| Bytac HDPE                        | 146                                    | 289             | 435            |                                      |                                          |                                  |                     |
| Bytac HDPE                        | 133                                    | 185             | 318            |                                      |                                          |                                  |                     |
| Bytac HDPE                        | 165                                    | 233             | 398            |                                      |                                          |                                  |                     |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng PETN on Nomex by ELECTROSTATIC swabbing | Total ng PETN recovered from 500 ng | Percent Recovery % |
|-----------------------------------|----------------------------------------|-----------------|----------------|------------------------------------------|----------------------------------|---------------------|
| Bytac HDPE                        | 151                                    | 122             | 142            | 415                                     |                                  | 34                  |
| Bytac HDPE                        | 221                                    | 52              | 154            | 426                                     |                                  | 36                  |
| Bytac HDPE                        | 99                                     | 127             | 95             | 321                                     |                                  | 30                  |
| Bytac HDPE                        | 22                                     | 16              | 281            | 319                                     |                                  | 88                  |
| Bytac HDPE                        | 81                                     | 217             | 127            | 425                                     |                                  | 30                  |
| Bytac HDPE                        | 73                                     | 196             | 186            | 455                                     |                                  | 41                  |
Table 1.17. Nomex contact and electrostatic swabbing for TNT from HDPE
Electrostatic swabs charged to -9.23 kV, -8.74 kV, and -10.16 kV at RH 40%.
TNT was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng TNT out of 500ng |
|----------------------------------|----------------------------------------|---------------------|
| HDPE                             | --                                     | 441                 |
| HDPE                             | --                                     | 499                 |
| HDPE                             | --                                     | 491                 |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng TNT recovered from 500 ng |
|----------------------------------|----------------------------------------|-----------------|----------------|----------------------------------|
| Bytac                            | HDPE                                   | 57              | 475            | 532                              |
| Bytac                            | HDPE                                   | 90              | 363            | 453                              |
| Bytac                            | HDPE                                   | 0               | 443            | 443                              |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng TNT on Nomex by CONTACT swabbing | ng TNT on Nomex by ELECTROSTATIC swabbing | Total ng TNT recovered from 500 ng | Percent Recovery % |
|----------------------------------|----------------------------------------|-----------------|----------------|-------------------------------------|-------------------------------------------|-------------------------------|-------------------|
| Bytac                            | HDPE                                   | 0               | 42             | 354                                 |                                           | 397                           | 89                |
| Bytac                            | HDPE                                   | 78              | 40             | 354                                 |                                           | 472                           | 75                |
| Bytac                            | HDPE                                   | 95              | 180            | 205                                 |                                           | 480                           | 43                |
| Bytac                            | HDPE                                   | 93              | 119            | 294                                 |                                           | 507                           | 58                |
| Bytac                            | HDPE                                   | 92              | 30             | 394                                 |                                           | 516                           | 76                |
| Bytac                            | HDPE                                   | 0               | 65             | 355                                 |                                           | 420                           | 84                |
Cotton

Direct contact swabbing of cotton was compared to electrostatic swabbing using the standard dry-transfer technique and inductive charging method. Three analytes were examined: PETN (Table 1.18), TNT (Table 1.19), and RDX (Table 1.20). Pickup efficiency is on the order of 20 to 30%. This suggested that the electrostatic swabbing pickup is less dependent on analyte and more dependent on the surface of a substrate.

Table 1.18. Nomex contact and electrostatic swabbing for PETN from cotton
Electrostatic swabs charged to -12.34 kV, -11.49 kV, & -13.69 kV at RH 25%. PETN was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng PETN out of 500ng |
|----------------------------------|--------------------------------------|----------------------|
| Cotton                           | --                                   | 421                  |
| Cotton                           | --                                   | 414                  |
| Cotton                           | --                                   | 426                  |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng PETN recovered from 500ng |
|----------------------------------|--------------------------------------|----------------|----------------|-----------------------------------|
| Bytac                            | Cotton                               | 21             | 507            | 529                               |
| Bytac                            | Cotton                               | 5              | 435            | 439                               |
| Bytac                            | Cotton                               | 1              | 397            | 399                               |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng PETN on Nomex by CONTACT swabbing | ng PETN on Nomex by ELECTROSTATIC swabbing | Total ng PETN recovered from 500ng | Percent Recovery % |
|----------------------------------|--------------------------------------|----------------|----------------|--------------------------------------|------------------------------------------|----------------------------------|-------------------|
| Bytac                            | Cotton                               | 1              | 337            | 74                                   | 412                                      | 18                              |
| Bytac                            | Cotton                               | 0              | 304            | 51                                   | 355                                      | 15                              |
| Bytac                            | Cotton                               | 12             | 297            | 71                                   | 381                                      | 19                              |
| Bytac                            | Cotton                               | 20             | 411            | 90                                   | 521                                      | 17                              |
| Bytac                            | Cotton                               | 30             | 307            | 154                                  | 490                                      | 31                              |
| Bytac                            | Cotton                               | 2              | 334            | 204                                  | 540                                      | 38                              |

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Table 1.19. Nomex contact and electrostatic swabbing for TNT from cotton
Electrostatic swabs charged to -8.99 kV, -10.23 kV, & -11.14 kV at RH 35%.
TNT was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng TNT out of 500ng | Total ng TNT recovered from 500ng |
|----------------------------------|----------------------------------------|--------------------|----------------------------------|
| Cotton                           | --                                     | 480                |                                  |
| Cotton                           | --                                     | 578                |                                  |
| Cotton                           | --                                     | 548                |                                  |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng TNT on Nomex by CONTACT swabbing | ng TNT on Nomex by ELECTROSTATIC swabbing | Total ng TNT recovered from 500ng | Percent Recovery % |
|----------------------------------|----------------------------------------|-----------------|----------------|-------------------------------------|------------------------------------------|-------------------------------|-------------------|
| Bytac                            | Cotton                                | 28              | 448            | 476                                 | 11                                       | 519                           | 11                |
| Bytac                            | Cotton                                | 0               | 489            | 489                                 | 19                                       | 578                           | 19                |
| Bytac                            | Cotton                                | 14              | 443            | 457                                 | 14                                       | 500                           | 14                |

Table 1.20. Nomex contact and electrostatic swabbing for RDX from cotton
Electrostatic swabs charged to -10.21 kV, -11.44 kV, & -12.66 kV at RH 30%
RDX was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng RDX out of 500ng | Total ng RDX recovered from 500ng |
|----------------------------------|----------------------------------------|---------------------|----------------------------------|
| Cotton                           | --                                     | 535                 |                                  |
| Cotton                           | --                                     | 460                 |                                  |
| Cotton                           | --                                     | 434                 |                                  |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng RDX recovered from 500ng |
|----------------------------------|----------------------------------------|-----------------|----------------|-------------------------------|
| Bytac                            | Cotton                                | 123             | 367            | 490                           |
| Bytac                            | Cotton                                | 109             | 326            | 435                           |
| Bytac                            | Cotton                                | 76              | 387            | 463                           |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng RDX on Nomex by CONTACT swabbing | ng RDX on Nomex by ELECTROSTATIC swabbing | Total ng RDX recovered from 500ng | Percent Recovery % |
|----------------------------------|----------------------------------------|-----------------|----------------|-------------------------------------|------------------------------------------|-------------------------------|-------------------|
| Bytac                            | Cotton                                | 127             | 296            | 87                                 | 510                                       | 427                           | 17                |
| Bytac                            | Cotton                                | 82              | 290            | 98                                 | 470                                       | 482                           | 21                |
| Bytac                            | Cotton                                | 137             | 252            | 81                                 | 471                                       | 512                           | 17                |
| Bytac                            | Cotton                                | 140             | 263            | 87                                 | 490                                       | 577                           | 18                |
| Bytac                            | Cotton                                | 68              | 284            | 126                                | 478                                       | 504                           | 26                |
| Bytac                            | Cotton                                | 63              | 307            | 77                                 | 448                                       | 525                           | 17                |
**Ohio Travel Bag Zipper**

In comparison to some of the other substrates which are flat surfaces, the Ohio zipper is a small pull tab with many grooves (Figure 1.17). According to the manufacturer, the pull tab is made of a polyurethane resin.

![Ohio Travel Bag Zipper](image)

Figure 1.17. Ohio Travel Bag Zipper

The results obtained in Table 1.21 show that electrostatic swabs outperformed contact swabbing for PETN. In the TNT study, the dry transfer was less efficient than in the PETN study, though the outcome remained the same with electrostatic swabs outperforming contact (Table 10.22). In the RDX study, to a lesser extent electrostatic swabs outperformed contact (Table 10.23). The third contact swab did not have a sufficient dry transfer which may have skewed the results. Despite the many grooves of the pull tab, standard deviation of percent recovery was quite consistent amongst the three analytes.
Table 1.21. Nomex contact and electrostatic swabbing for PETN from Ohio Zipper

Electrostatic swabs charged to -11.14 kV, -9.43 kV, & -10.87 kV at RH 30%

PETN was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng PETN out of 500ng | remaining on S1 | remaining on S2 | Total ng PETN recovered from 500ng |
|----------------------------------|----------------------------------------|---------------------|----------------|---------------|----------------------------------|
| Ohio Zipper                      | --                                     | 477                 |                |               |                                  |
| Ohio Zipper                      | --                                     | 441                 |                |               |                                  |
| Ohio Zipper                      | --                                     | 461                 |                |               |                                  |

Table 1.22. Nomex contact and electrostatic swabbing for TNT from Ohio Zipper

Electrostatic swabs charged to -7.55 kV, -10.13 kV, & -9.61 kV at RH 30%

TNT was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng TNT out of 500ng | remaining on S1 | remaining on S2 | Total ng TNT recovered from 500ng |
|----------------------------------|----------------------------------------|---------------------|----------------|---------------|----------------------------------|
| Ohio Zipper                      | --                                     | 429                 |                |               |                                  |
| Ohio Zipper                      | --                                     | 545                 |                |               |                                  |
| Ohio Zipper                      | --                                     | 478                 |                |               |                                  |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng TNT recovered from 500ng |
|----------------------------------|----------------------------------------|----------------|---------------|----------------------------------|
| Bytac Ohio Zipper                | 94                                     | 411             | 505           |                                  |
| Bytac Ohio Zipper                | 106                                    | 369             | 475           |                                  |
| Bytac Ohio Zipper                | 78                                     | 469             | 547           |                                  |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng TNT on Nomex by CONTACT swabbing | ng TNT on Nomex by ELECTROSTATIC swabbing | Total ng TNT recovered from 500ng | Percent Recovery % |
|----------------------------------|----------------------------------------|----------------|---------------|----------------------------------|------------------------------------------|---------------------------------|-------------------|
| Bytac Ohio Zipper                | 103                                    | 257            | 139           | 499                             |                                          |                                | 28                |
| Bytac Ohio Zipper                | 72                                     | 265            | 133           | 470                             |                                          |                                | 28                |
| Bytac Ohio Zipper                | 92                                     | 258            | 164           | 514                             |                                          |                                | 32                |
| Bytac Ohio Zipper                | 92                                     | 260            | 165           | 517                             |                                          |                                | 32                |
| Bytac Ohio Zipper                | 44                                     | 264            | 202           | 510                             |                                          |                                | 40                |
| Bytac Ohio Zipper                | 59                                     | 249            | 189           | 497                             |                                          |                                | 38                |
Table 1.23. Nomex contact and electrostatic swabbing for RDX from Ohio Zipper
Electrostatic swabs charged to -12.61 kV, -10.47 kV, & -7.36 kV at RH 30%
RDX was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng RDX out of 500ng | Total ng RDX recovered from 500 ng |
|----------------------------------|--------------------------------------|----------------------|----------------------------------|
| Ohio Zipper                      | --                                   | 540                  | 502                              |
| Ohio Zipper                      | --                                   | 556                  | 502                              |
| Ohio Zipper                      | --                                   | 426                  | 502                              |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng RDX recovered from 500 ng |
|----------------------------------|--------------------------------------|----------------|----------------|----------------------------------|
| Bytac                            | Ohio Zipper                          | 3              | 498            | 502                              |
| Bytac                            | Ohio Zipper                          | 0              | 389            | 389                              |
| Bytac                            | Ohio Zipper                          | 16             | 534            | 550                              |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng RDX on Nomex by CONTACT swabbing | ng RDX on Nomex by ELECTROSTATIC swabbing | Total ng RDX recovered from 500 ng | Percent Recovery % |
|----------------------------------|--------------------------------------|----------------|----------------|----------------------------------|------------------------------------------|----------------------------------|-------------------|
| Bytac                            | Ohio Zipper                          | 6              | 314            | 180                             | 180                                      | 500                              | 36                |
| Bytac                            | Ohio Zipper                          | 0              | 274            | 206                             | 206                                      | 480                              | 43                |
| Bytac                            | Ohio Zipper                          | 197            | 157            | 168                             | 168                                      | 522                              | 32                |
| Bytac                            | Ohio Zipper                          | 1              | 217            | 278                             | 278                                      | 496                              | 56                |
| Bytac                            | Ohio Zipper                          | 9              | 295            | 175                             | 175                                      | 479                              | 37                |
| Bytac                            | Ohio Zipper                          | 16             | 308            | 208                             | 208                                      | 532                              | 39                |

Aluminum foil

Dry transfer is often claimed to be more representative of actual explosive residue transfer than direct deposit via solvent [18]. To compare the efficiency of dry transfer to direct deposit of an analyte and to compare contact swabbing to non-contact electrostatic swabbing, the following experiments were performed. Aluminum foil was the substrate; PETN, the analyte; and Nomex, the swab. To evaluate just the transfer method, three aluminum substrates were prepared by directly depositing 500 ng of PETN from acetone solution of 100 ng/µL (Table 1.24). An additional three were prepared by first direct depositing the PETN solution onto Bytac® which then was used to dry transfer the PETN onto the aluminum foil (Table 1.25). Both sets of foil were extracted with 1 mL of 50:50 ACN/H₂O and analyzed on the (LC/MS).
While mass balance is closer to 500 ng for direct deposit Table 1.24, swabs did not recover as much PETN in comparison to the dry transfer method in Table 1.25. In addition, electrostatically enhanced swabs performed better in the dry transfer study. This is to be expected as a residue which was direct deposited via solvent can settle in the grooves of a substrate as solvent evaporates. This is in opposition to dry transfer where the analyte tends to adhere to the more exposed surface. In the case of TNT from aluminum foil, Table 1.26 shows that the recovery for electrostatic swabs outperformed contact swabbing. In addition to a higher recovery on the swab, dry transfer was more efficient with almost all of the analyte on Bytac® being transferred to the substrate. Swabs can only pickup what has been transferred to the substrate, so the efficiency of dry transfer is an important metric in these studies. In the RDX study from aluminum foil, the data in Table 1.27 shows an instance where contact swabs outperformed electrostatic swabs. A high total recovery of RDX on the first contact swab, 58% (390/676 ng), is suspect.

Table 1.24. Nomex contact and electrostatic swabbing for PETN from Al foil using the direct deposit method

| Substrate (S1) for direct deposit | ng PETN of 500ng remaining on Al Foil after | ng PETN on Nomex by CONTACT swabbing | ng PETN on Nomex by ELECTROSTATIC swabbing | Total Foil ng PETN recovered from 500 | Percent Recovery % |
|----------------------------------|------------------------------------------|-------------------------------------|-------------------------------------------|-------------------------------------|-------------------|
| Al Foil                          | 304                                      | 114                                 | 418                                       | 27                                  |
| Al Foil                          | 484                                      | 58                                  | 542                                       | 11                                  |
| Al Foil                          | 456                                      | 41                                  | 497                                       | 8                                   |
| Al Foil                          | 393                                      | 25                                  | 418                                       | 6                                   |
| Al Foil                          | 379                                      | 37                                  | 416                                       | 9                                   |
| Al Foil                          | 428                                      | 43                                  | 471                                       | 9                                   |
Table 1.25. Nomex contact and electrostatic swabbing for PETN from Al foil

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng PETN out of 500ng | Total Al Foil ng PETN recovered from 500ng |
|----------------------------------|---------------------------------------|---------------------|-----------------------------------------|
| Al Foil                         | --                                    | 429                 |                                         |
| Al Foil                         | --                                    | 361                 |                                         |
| Al Foil                         | --                                    | 359                 |                                         |

Table 1.26. Nomex contact and electrostatic swabbing for TNT from Al foil

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng TNT out of 500ng | Total ng TNT recovered from 500ng |
|----------------------------------|---------------------------------------|---------------------|-------------------------------|
| Al Foil                         | --                                    | 472                 |                               |
| Al Foil                         | --                                    | 423                 |                               |
| Al Foil                         | --                                    | 425                 |                               |

Table 1.26. Nomex contact and electrostatic swabbing for TNT from Al foil

TNT was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng TNT out of 500ng | Total ng TNT recovered from 500ng |
|----------------------------------|---------------------------------------|---------------------|-------------------------------|
| Bytac                            | Al Foil                               | 0                   | 534                           |
| Bytac                            | Al Foil                               | 0                   | 486                           |
| Bytac                            | Al Foil                               | 0                   | 477                           |

Table 1.26. Nomex contact and electrostatic swabbing for TNT from Al foil

TNT was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng TNT out of 500ng | Total ng TNT recovered from 500ng |
|----------------------------------|---------------------------------------|---------------------|-------------------------------|
| Bytac                            | Al Foil                               | 0                   | 247                           | 137 | 384 | 36 |
| Bytac                            | Al Foil                               | 16                  | 281                           | 89  | 386 | 23 |
| Bytac                            | Al Foil                               | 11                  | 167                           | 154 | 332 | 46 |
| Bytac                            | Al Foil                               | 0                   | 134                           | 283 | 417 | 68 |
| Bytac                            | Al Foil                               | 8                   | 122                           | 235 | 365 | 64 |
| Bytac                            | Al Foil                               | 0                   | 159                           | 187 | 346 | 54 |
Table 1.27. Nomex contact and electrostatic swabbing for RDX from Al foil
Electrostatic swabs charged to -7.36 kV, -7.99 kV, & -9.11 kV at RH 40%
RDX was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng RDX out of 500ng |
|----------------------------------|---------------------------------------|-------------------|
| Al Foil                          | --                                    | 534               |
| Al Foil                          | --                                    | 530               |
| Al Foil                          | --                                    | 540               |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng RDX recovered from 500 ng |
|----------------------------------|---------------------------------------|----------------|----------------|---------------------------------|
| Bytac                            | Al Foil                               | 97             | 438            | 535                             |
| Bytac                            | Al Foil                               | 102            | 404            | 506                             |
| Bytac                            | Al Foil                               | 73             | 422            | 495                             |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng RDX on Nomex by CONTACT swabbing | ng RDX on Nomex by ELECTROSTATIC swabbing | Total ng RDX recovered from 500 ng | Percent Recovery % |
|----------------------------------|---------------------------------------|----------------|----------------|-----------------------------------|---------------------------------------------|---------------------------------|-------------------|
| Bytac                            | Al Foil                               | 89             | 196            | 390                               | 676                                         | 58                             |
| Bytac                            | Al Foil                               | 36             | 346            | 137                               | 519                                         | 26                             |
| Bytac                            | Al Foil                               | 0              | 249            | 259                               | 508                                         | 51                             |
| Bytac                            | Al Foil                               | 79             | 359            | 60                                | 499                                         | 12                             |
| Bytac                            | Al Foil                               | 53             | 326            | 136                               | 515                                         | 26                             |
| Bytac                            | Al Foil                               | 50             | 316            | 176                               | 542                                         | 32                             |
**Ballistic Nylon**

In the ballistic nylon study, excess methanol >10 mL was necessary to achieve a satisfactory quantification due to its absorption of solvent. The percent recovery in both contact and electrostatic swabbing was low, contact outperformed electrostatic swabs (Table 1.28).

**Table 1.28. Nomex contact and electrostatic swabbing for PETN from Ballistic Nylon**

Electrostatic swabs charged to -7.16 kV, -6.99 kV, & -9.71 kV at RH 40%

PETN was deposited from a solution of acetone

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | ng PETN out of 500ng |
|----------------------------------|---------------------------------------|---------------------|
| Ballistic Nylon                  | --                                    | 575                 |
| Ballistic Nylon                  | --                                    | 626                 |
| Ballistic Nylon                  | --                                    | 583                 |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng PETN recovered from 500 ng |
|----------------------------------|---------------------------------------|----------------|----------------|-------------------------------|
| Bytac                            | Ballistic Nylon                      | 31             | 460            | 492                           |
| Bytac                            | Ballistic Nylon                      | 54             | 473            | 527                           |
| Bytac                            | Ballistic Nylon                      | 6              | 445            | 451                           |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | ng PETN on Nomex by CONTACT swabbing | ng PETN on Nomex by ELECTROSTATIC swabbing | Total ng PETN recovered from 500 ng | Percent Recovery % |
|----------------------------------|---------------------------------------|----------------|----------------|-------------------------------------|------------------------------------------|-------------------------------|-------------------|
| Bytac                            | Ballistic Nylon                      | 15             | 325            | 51                                  | 391                                      | 13                            |                   |
| Bytac                            | Ballistic Nylon                      | 5              | 305            | 96                                  | 406                                      | 24                            |                   |
| Bytac                            | Ballistic Nylon                      | 20             | 342            | 80                                  | 442                                      | 18                            |                   |
| Bytac                            | Ballistic Nylon                      | 4              | 406            | 67                                  | 477                                      | 14                            |                   |
| Bytac                            | Ballistic Nylon                      | 6              | 406            | 24                                  | 436                                      | 5                             |                   |
| Bytac                            | Ballistic Nylon                      | 10             | 388            | 33                                  | 431                                      | 8                             |                   |
**Packing Tape**

The objective in determining pickup from polypropylene packing tape was to examine the non-sticky side. It was necessary to remove the adhesive backing for subsequent extraction of the analyte. However, no amount of extraction completely removed the adhesive. FTIR analysis (Figure 1.18) revealed the tape was made of polypropylene. Therefore, polypropylene was used as substrate S2. Data in Table 1.29 shows PETN deposited on polypropylene resulted in recoveries <100%.

![Figure 1.18. FTIR spectrum of authentic packing tape sample (Left) surrogate (Right)](image)

**Table 1.29 Nomex contact and electrostatic swabbing for PETN from packing tape**

Electrostatic swabs charged to -7.58 kV, -11.52 kV, & -10.31 kV at RH 20%

PETN was deposited from a solution of acetone

| Substrate (S1) | Substrate (S2) | ng PETN out of 500ng |
|---------------|---------------|----------------------|
| TAPE          | --            | 120                  |
| TAPE          | --            | 24                   |
| TAPE          | --            | 67                   |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng PETN recovered from 500 ng |
|----------------------------------|----------------------------------------|----------------|----------------|------------------------------------|
| Bytac                            | TAPE                                   | 160            | 26             | 187                                |
| Bytac                            | TAPE                                   | 64             | 114            | 178                                |
| Bytac                            | TAPE                                   | 334            | 5              | 339                                |

| Substrate (S1) for direct deposit | Substrate (S2) onto which dry transfer | remaining on S1 | remaining on S2 | Total ng PETN on Nomex by CONTACT swabbing | Total ng PETN on Nomex by ELECTROSTATIC swabbing | Percent Recovery % |
|----------------------------------|----------------------------------------|----------------|----------------|---------------------------------------------|---------------------------------------------|-------------------|
| Bytac                            | TAPE                                   | 280            | 3              | 25                                          | 308                                         | 8                 |
| Bytac                            | TAPE                                   | 371            | 12             | 29                                          | 412                                         | 7                 |
| Bytac                            | TAPE                                   | 130            | 4              | 78                                          | 212                                         | 37                |
| Bytac                            | TAPE                                   | 148            | 6              | 52                                          | 206                                         | 25                |
| Bytac                            | TAPE                                   | 241            | 5              | 50                                          | 295                                         | 17                |
| Bytac                            | TAPE                                   | 429            | 2              | 17                                          | 447                                         | 4                 |
Vinyl/ Nylon 1000

Simulated leather with flannel-backed vinyl, as well as the clear sheeting vinyl, resulted in matrix interference on the LC/MS. The extraction of vinyl in various solvents, acetonitrile, isopropanol, and methanol, decreased the signal response of the analyte, PETN, and gave false values in quantification. It was attempted to extract this matrix, and use the matrix as the solvent, matrix-matched standards, in order to eliminate this issue. The linear regression correlation ($R^2$) was unacceptable for quantification, so there is no data in quantifying from dry transfer for the vinyl substrate. The same conflict occurred with Nylon 1000, though the black color was extracted in the solvent, and initially this seemed to be the interferent. After obtaining white Nylon 1000 and attempting the same extraction, the interferent was still present. No further attempts to quantify on LC/MS with these substrates occurred in this study.

Explosive Trace Detectors (ETD)

In this section the feasibility of using electrostatic non-contact swabbing methods with airport ETDs is verified. Shown in Figures 1.19 and 1.20 are responses of increasing amounts of PETN to an ion mobility spectrometer in NITRO and PETN response modes. PETN response is hyperbolic, approaching maximum response at higher amounts of PETN. This suggests that the detector is saturated with PETN. Figure 1.21 shows similar results for ammonium nitrate on IMS in NITRO mode.
Figure 1.19. IMS signal response for NITRO for increasing concentrations of PETN

Figure 1.20. IMS signal response for PETN for increasing concentrations of PETN

Figure 1.21. IMS signal response for NITRO for increasing concentrations of AN
In Table 1.30, the dry transfer method was used to deposit 100 ng of PETN, 100 ng TNT, or 500 ng AN on the various substrates listed in the substrate 2 column. These substrates were swabbed with either an electrostatically enhanced swab or a contact swab; the swab was presented to the ETD, and the magnitude of the response was recorded.

Table 1.30. IMS responses of contact vs electrostatically enhanced swabs

| Substrate 2 | Charge (-kV) or Contact | PETN Detection | AN Detection | TNT Detection |
|-------------|------------------------|----------------|--------------|--------------|
| HDPE        | 6.91 PETN              | 7.02           | 1.51         | 9.45 2.44    | 8.01 4.27    |
|             | Contact                | 1.71 2         | Contact      | Contact      | Contact      |
| Cotton      | 5.24 PETN              | 4.43 0         | 1.13 10.23   | 2.31 1.00    | 9.84 3.04    |
|             | Contact                | 1.42 2         | Contact      | Contact      | Contact      |
| Al Foil     | 5.20, 7.64 PETN        | 3.76 2         | 1.64 8.31    | 1.24 1.03    | 8.86 2.11    |
|             | Contact                | 1.13 3         | Contact      | Contact      | Contact      |
| Nylon 1000  | 9.46 PETN              | 1.42 0         | 1.32 10.23, 11.17 | 1.08 1     |
|             | Contact                | 2 NITRO        | Contact      | Contact      | Contact      |
| PC          | 7.2, 7.8, 6.5          | X X 3          | 6.9, 9.9, 7.5 | X X 3       |
|             | Contact                | X X 3          | Contact      | X X 3       |
| Ballistic Nylon | 5.8, 5.9, 6.0      | X X 3          | 7.5, 8.7, 7.1 | X X 3       |
|             | Contact                | X X 3          | Contact      | X X 3       |
| PTFE        | 5.8, 6.3, 6.0          | X X 3          | 7.3, 6.5, 9.5 | NITRO X 3   |
|             | Contact                | X X 3          | Contact      | NITRO X 3   |
| ABS         | 8.53 X X 3             | 8.74, 8.53     | NITRO 1.22   | 1            |
|             | Contact                | X X 3          | Contact      | X X 3       |
| Vinyl       | 10.33 PETN             | 1.58 0         | 6.95, 9.31   | NITRO 2.01   |
|             | Contact                | X X 3          | Contact      | X X 3       |

The results show electrostatically enhanced swabs achieved higher response magnitudes than contact swabs. In the cases of ballistic nylon, polycarbonate (PC), PTFE, and ABS neither electrostatic nor contact swabbing was able to elicit responses from the instrument at this concentration. This trend agrees with LC/MS quantification showing that neither electrostatic nor contact swabbing had a greatly enhanced performance. In the vinyl and Nylon 1000 experiments, electrostatic swabs retained a higher amount of analyte than contact. Results agree with literature that transfer efficiency is poor to hard plastic [24].
**C-4 Fingerprints: Comparing positive and negative voltages**

In order to determine if the sign of the voltage had an effect on sorption of explosive residue, a simple test was completed (Table 1.31). With increasing magnitude, whether positive or negative, response magnitude increases, the only outlier being the first test of +4.78 kV where the response magnitude is the highest. Two swabs (fiberglass coated Teflon) were stacked on the grounding plate. The swabs were charged for 5 seconds at -20 kV from 2 inches away from the pinner at 40% RH. Single C-4 fingerprints were made with index fingers of various participants on a cellulose substrate (filter paper). Charges were recorded and swabs approached fingerprints from 10 mm above the substrate. Swabs were tested in the Morpho Itemiser DX ETD. Additionally, controls were performed where charged swabs went directly into the inlet to insure no false alarms came from charging. These results verified that both positive and negative charging results in a response from the IMS.

**Table 1.31. Positive and negative charging to pick up RDX from a C-4 fingerprint**

| CHARGE (KV) | RESPONSE MAGNITUDE |
|-------------|---------------------|
| +4.78       | 4.27 2.67           |
| -10.43      | 3.92 2.30           |
| +2.79       | 1.17 0.92           |
| -8.69       | 2.91 1.42           |
| +6.76       | 3.88 2.11           |
| **CONTROLS WITH NO C4** |           |
| +5.05       |                     |
| -6.39       |                     |
CONCLUSION

Commercial swabs were charged using the inductive method. This charging method was optimized for the surface on which charging occurred and length of charging time (5 sec). Several commercial swab types were tested in humidity ranging 0 to 80% RH. As humidity increased charge imparted to the swabs decreased. The negatively charged swabbing material still developed enough charge to enhance particle pickup. Cotton swabs charged positively, and rapidly lost this charge. Storage and stacking methods were tested to determine if swabs could be packaged charged; this did not seem to be the case.

Methods of applying the analyte to the substrate surface were examined. Direct deposit of the analyte from solution with subsequent evaporation of the solvent was compared to the “dry transfer” method. Dry transfer and Nomex swabs were used in all quantitative comparison studies of contact versus non-contact, electrostatic swabbing. Using the dry transfer method, thirteen substrates were analyzed; and analytical protocols, developed to quantify three different organic explosives in comparing contact to electrostatic swabbing. In the case where quantification of the analyte pickup was not amenable to LC methods, a commercial ETD and Teflon-coated fiberglass swabs were used to compare the relative pickup by the two swabbing methods.

Findings, summarized in Tables 1.32 and 1.33 indicate that in most cases, electrostatically enhanced swabs were more effective in collecting explosives particles than contact swabbing. Use of this technique would decrease the invasiveness of swabbing and possibly lower false alarms by eliminating the pickup of some types of
contaminants. It is anticipated at check point, charging would increase sample time by about 5 seconds and that humidity would be similar to that employed in this testing.

Table 1.32. Quantification as % Recoveries comparing pickup of explosives using contact vs electrostatic swabs at 5 to 40% RH

| Substrate | PETN | RDX | TNT |
|-----------|------|-----|-----|
| Polycarbonate | 13 3 38 25 | 13 4 39 19 | 3 1 22 13 |
| Cardboard | 24 8 46 16 | 26 15 33 22 | |
| Bytac | 11 3 20 8 | 26 15 33 22 | |
| ABS | 69 20 73 11 | 33 3 53 25 | |
| Teflon | 15 3 16 3 | 18 2 20 4 | 17 2 29 8 |
| High Density Polyethylene | 29 3 37 2 | 37 4 44 8 | 37 16 48 13 |
| Cotton | 35 10 62 6 | 45 13 23 8 | 29 5 34 5 |
| Zippers | 17 14 15 9 | 18 4 9 4 | |
| Al Foil (metal) | 15 3 16 3 | 18 2 20 4 | 17 2 29 8 |
| Packing tape | 24 8 46 16 | 26 15 33 22 | |
| Ballistic Nylon | 18 4 9 4 | 17 14 15 9 | |
| Nylon 1000 | 17 14 15 9 | 18 4 9 4 | |
| Vinyl | 17 14 15 9 | 18 4 9 4 | |

Table 1.33. IMS response comparing pickup of explosives on contact vs electrostatic swabs

| Substrate | PETN Detection | AN Detection | TNT Detection |
|-----------|----------------|--------------|---------------|
| PETN | number repeats required | response | number repeats required | response | number repeats required | response |
| AN | number repeats required | response | number repeats required | response | number repeats required | response |
| TNT | number repeats required | response | number repeats required | response | number repeats required | response |

| Substrate | PETN | AN | TNT |
|-----------|------|----|-----|
| HDPE | 7 PETN | 9 NITRO | 8 TNT |
| Cotton | 5 PETN | 10 NITRO | 10 TNT |
| Al Foil | 7.00 PETN | 8 NITRO | 7 TNT |
| Nylon 1000 | 9 PETN | 11 NITRO | 11 |
| PC | 7 X | 8 X | 8 |
| Ballistic Nylon | 6 X | 7 X | 7 |
| PTFE | 6 X | 9 NITRO | 9.00 NITRO |
| ABS | 9 X | Contact X X 3 | 3 |
| Vinyl | 10 PETN | 9 NITRO | 9 |

response level: high, medium, low
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Manuscript 2

Potential Biocides: Polymer Packaging of Iodine containing Pyrotechnics

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ABSTRACT

Iodine-producing pyrotechnics have been investigated as biocides against biological warfare agents [1-4]. For controlled application and dispersion of these formulations in the field, polyurethane matrixes were examined as binders. To that end, five energetic polyols containing energetic moieties nitro (–NO₂) and/or azide (–N₃) were synthesized and characterized. These were used as partial replacements for triethanolamine (TEOA) in its reaction with toluene diisocyanate (TDI) to produce polyurethane. The most promising of these polyurethane foams were mixed with a pyrotechnic formulation (90/10 Ca(IO₃)₂/Al powder) to test for heat and iodine output. Despite high solids loading (>70%) the foam cured without significant decrease in expansion compared to the simple polyurethane (about 9 fold). Without polyurethane, a 90/10 formulation of Ca(IO₃)₂/Al resisted ignition, but in the presence of the foam binder it was highly flammable. Addition of the energetic monomer did not greatly improve the excellent heat output of the standard polyurethane foam, but it improved iodine output.
INTRODUCTION

The threat of biological weapons, specifically spores of *Bacillus anthracis* species, are of concern to those charged with homeland security. Although the exact kill mechanism is unknown, current research efforts suggest that heat and iodine gases can act as a biocide causing DNA damage and increasing the kill-rate in spores [3-4]. Previous work examined the heat and iodine outputs of various fuels and oxides of iodine mixtures [5]. For controlled application and dispersion of the biocidal formulations in the field, these fuel/oxidizer mixtures require a binder. For a quick and thorough application of the biocidal formulation, a sprayable binder was considered best. The properties desired in a sprayable binder would include rapid curing (less than 10 seconds) with significant expansion and acceptable mechanical properties so that high solids loading could be achieved. It was determined that polyurethane foams met these needs. Because polyurethane formations are based on combining a diisocyanate with a polyol to produce a urethane linkage, (Figure 2.1) a number of modifications can be applied by changing one of the monomers [6]. Functionalizing polymers with nitro or azide groups is the usual approach to creating energetic binders [7-9]. Polyurethane foams were exclusively investigated in this study.

![Figure 2.1. general urethane linkage schematic](image)

Figure 2.1. general urethane linkage schematic
EXPERIMENTAL METHODS

Materials

All chemical reagents and analytical grade solvents were purchased from, Acros Organics, Alpha Aesar, Fisher Scientific, TCI, or STREM and used without further purification. Particle size of the calcium iodate was 70 to 150 μm; and the aluminum, from Obron, was 23 μm. To lower the surface tension during polymer preparation, promote uniform cell structure, and increase expansion, surfactant (Triton™ GR-7M) provided by DOW Chemical was used at 1 wt % solution in pentane.

Fourier Transform-Infrared Spectrometer (FTIR)

Infrared spectra were measured with a Thermo Scientific Nicolet 6700 spectrometer equipped with a Smart iTR diamond ATR. FTIR spectra were recorded at ambient temperature. Background and spectra were collected in ranges of 4000-650 cm⁻¹.

Thermal Measurements

Melting points, decomposition temperatures, and enthalpies were determined using a TA Q100 for differential scanning calorimetry (DSC), calibrated against an indium standard, heating at 20 °C min⁻¹ under nitrogen flow of 50 mL/min. Hermetic aluminum pans were used for monomers, and glass sealed capillaries, for polymers. Polymer decomposition was monitored with a TA Q600 Simultaneous DSC/TGA (SDT) instrument; samples were held in open alumina pans, with heating rate 20 °C min⁻¹ and nitrogen flow of 300 mL min⁻¹.

Liquid Chromatography/ Mass Spectrometer (LCMS)

To determine mass spectra, each compound was dissolved in methanol to make a 1mg/mL solution and then serially diluted to 10 μg/mL. This methanol solution was
infused into Thermo Scientific LTQ Orbitrap XL™ mass spectrometer (MS) at a rate of 5 μL/min using electrospray ionization source in negative mode. The ionization source and ion optics parameters were as follows: sheath gas 8, auxiliary gas 1, spray voltage 4.0 kV, capillary temperature 275 °C, capillary voltage -1 V, tube lens -33.8 V, multipole 00 offset 2.5 V, lens 0 4.5 V, multipole 0 offset 4.75 V, lens 1 20.0 V, gate lens 64.0 V, multiple 1 offset 8.0 V, multipole RF amplitude 400.0 V, front lens 4.75 V. The mass spectra were collected using a full scan in ranges of 70 to 800 AMU (atomic mass units).

**Monomers**

2-(Hydroxymethyl)-2-nitropropane-1,3-diol (TMNM, 1) [10]

TMNM (1) was prepared by mixing nitromethane (17.9 g, 0.293 mol) in a potassium hydroxide (0.49 g, 8.7 mol) methanol (45 mL)/dichloromethane (2 mL) solution in a 250 mL round-bottom flask. The flask was cooled to 5°C and portions of 28g, 0.933mol paraformaldehyde (37% w/v in water) solution was stirred in over 30 minutes. The mixture was heated to 40°C, refluxed 2 hours, cooled to room temperature, and placed in a freezer overnight. The precipitate was collected by vacuum filtration, washed with hexanes, and dried in vacuum oven overnight at 50 °C to yield Compound 1 26.81g, 60%, m.p. 150-4°C (Figure 2.2).

![Synthesis of 2-(Hydroxymethyl)-2-nitropropane-1,3-diol (TMNM, 1)](image-url)

Figure 2.2. Synthesis of 2-(Hydroxymethyl)-2-nitropropane-1,3-diol (TMNM, 1)
2,3-Bis(hydroxymethyl)-1,3-dinitrobutane-1,4-diol (TETRA, 2) [10]

Compound 1 was condensed with acetone to form the ketal, (2,2-dimethyl-5-nitro-1,3-dioxan-5-yl)methanol (2a), as follows. In a 250 mL round bottom flask Compound 1 (30.21 g, 0.2 mol) and acetone (36.31 g, 0.620 mol) were combined, stirred, and warmed until Compound 1 was fully dissolved. The mixture was cooled to 20°C in an ice bath, and BF$_3$ (48% in ether, 34.38 g, 0.243 mol) was added to the flask all at once. The mixture was briefly heated to 60°C (~6 minutes) and then poured into a 2L beaker containing saturated sodium bicarbonate solution (500 mL) and shaved ice (100 mL). The tan colored precipitate was collected by vacuum filtration, washed with water, and air dried to yield 35.07 g (80%) of Compound 2a, melting point 130-132°C.

The dimerized ketal,2,2,2’,2’-tetramethyl-5,5’-dinitro-5,5’-bi(1,3-dioxane) (2b), was prepared from Compound 2a (57.08 g, 0.3 mol) by placing it in 750 mL water in a 2L round-bottom flask and heating it at 50°C for 2.5 hours with sodium hydroxide solution (50% w/w, 49 g, 0.6 mol). The mixture was cooled to 20°C; sodium persulfate (146 g, 0.613 mol) was added over the course of an hour; and stirring was continued at room temperature for 24 hours at which time sodium hydroxide solution (50% w/w) was added until the pH reached 11-12. The precipitate was filtered, washed with cold hexanes, and air dried to yield 2,2,2’,2’-tetramethyl-5,5’-dinitro-5,5’-bi(1,3-dioxane), (35.05 g, 72% yield), Compound 2b, a tan solid with melting point of 129-130°C.

The 2,3-bis(hydroxymethyl)-1,3-dinitrobutane-1,4-diol, Compound 2, was prepared in a 250 mL round-bottom flask by dissolving Compound 2b (17.2 g, 0.053 mol) in 190 mL of methanol and 15 mL of 12M HCl. The mixture was refluxed at 65°C for 40 minutes before the methanol and HCl were removed by rotary evaporation.
crude yield was 11.1 g (87%). The crude product compound 2 had a melting point of 100°C. It was recrystallized from 25 mL of hot ethyl acetate; the precipitate was rinsed with hexanes, and dried to yield 2,3-bis(hydroxymethyl)-1,3-dinitrobutane-1,4-diol, compound 2 8.37 g with a melting point of 108°C (Figure 2.3).

Figure 2.3. Synthesis of 2,3-Bis(hydroxymethyl)-1,3-dinitrobutane-1,4-diol (TETRA, 2)

2-(Azidomethyl)-2-nitropropane-1,3-diol (AZONITRO, 3) [11]

In a 250 mL round-bottom flask the ketal, (Compound 2a) (8.61 g, 45 mmol) was dissolved in pyridine (18 mL) and cooled to -15°C. To the stirred solution, tosyl chloride (9.173 g, 48 mol), dissolved in 13.5 mL dioxane, was added dropwise and allowed to stir overnight at room temperature. The mixture was poured over sodium bicarbonate (2.025 g) in 90 g of ice water. The white precipitate was isolated by vacuum filtration yielding 2,2-dimethyl-5-nitro-1,3-dioxan-5-yl 4-methylbenzenesulfonate (Compound 3a) 11.31 g (72% yield).

In a 250 mL round-bottom flask Compound 3a (9.22 g, 26.7 mmol) was dissolved in 75 mL of dimethylformamide; sodium azide (8.80 g, 135 mol) was added, and the mixture refluxed at 60°C for 24 hours. The slurry was poured over 135 g of ice and extracted with four aliquots of ethyl acetate (150 mL). The extracts were combined, washed with 4 portions of deionized water (150 mL), and dried over sodium sulfate. The sodium sulfate was removed by vacuum filtration; and the ethyl acetate, by rotary evaporation. Xylenes (50 mL) were added to create an azeotrope for the excess DMF;
they were removed together by rotary evaporation. Crystals of 5-(azidomethyl)-2,2-dimethyl-5-nitro-1,3-dioxane (Compound 3b) were removed from the round bottom to yield 5.1 g (88%).

In a 250 mL round-bottom flask, Compound 3b (4.9 g, 22.7 mmol) was combined with methanol (80mL) and 12M HCl (8mL) and refluxed at 60°C for 24 h. At room temperature, HCl and methanol were removed by rotary evaporation to produce dark amber oil, 2-(azidomethyl)-2-nitropropane-1,3-diol, Compound 3 with quantitative yield (4.2 g) (Figure 2.4).

![Diagram](image1.png)

**Figure 2.4. Synthesis of 2-(Azidomethyl)-2-nitropropane-1,3-diol (AZONITRO, 3)**

**2,2-Bis(Azidomethyl)propane-1,3-diol (BAMP, 4) [12-14]**

In a 250 mL round bottom flask, 2,2-bis(bromomethyl)propane-1,3-diol (Compound 4a) (2.8 g, 10.7 mmol) and sodium azide (1.74 g, 28.8 mmol) were dissolved in 20 mL DMSO. The solution was heated at 100 °C for 48 h. Then proportional amounts of water and brine were added (15 mL). The solution was extracted with three 20 mL portions of ethyl acetate. The ethyl acetate solution was dried with sodium sulfate, filtered, and remaining liquid removed by rotary evaporation yielding 1.90 g (95%) of light yellow oil Compound 4 (Figure 2.5).

![Diagram](image2.png)

**Figure 2.5. Synthesis of 2,2-Bis(Azidomethyl)propane-1,3-diol (BAMP, 4)**
**2,2-Dinitro-1,3-propanediol (DNPD, 5) [13-16]**

In a 500 mL round-bottom flask, 4.50 g of sodium hydroxide was dissolved in 200 mL of water. The ketal, Compound 1a, (10.15 g, 53 mmol) was added and stirred until dissolved. A solution of potassium ferricyanide (1.87 g) and sodium nitrite (14.7 g) in 30 mL of distilled water was added to the flask. The flask was put into an ice bath, and solid sodium persulfate (13.36 g) was added in portions while keeping the temperature below 30°C. The turbid solution was stirred for an additional 2 hours before the precipitate was collected by vacuum filtration, washed with cold distilled water, and air dried to yield 8.07 g of 2,2-dimethyl-5,5-dinitro-1,3-dioxane (86%) (Compound 5a), a light cream colored product with a melting point of 53-54°C.

To prepare Compound 5, in a 250 mL round-bottom flask, Compound 5a (8.07 g 39 mmol) was dissolved in 100 mL methanol and 14 mL of 12M HCl and heated at 60°C in an oil bath overnight. At room temperature, the HCl and methanol were removed by rotary evaporation; and the solid, dried to yield Compound 5, 5.20 g (80%) with a melting point of 135°C (Figure 2.6).

![Synthesis of 2,2-Dinitro-1,3-propanediol (DNPD, 5)](image-url)

Figure 2.6. Synthesis of 2,2-Dinitro-1,3-propanediol (DNPD, 5)
Polyurethane Foams

General Procedure of (TEOA-TDI) polyurethane foam synthesis

Part A consisted of toluene diisocyanate (TDI) (1 mL, 7.0 mmol) in 500 µL pentane to which 1 wt% DOW surfactant TRITON™ GR-7M. The two miscible liquids were stirred in a centrifuge tube. Part B consisted of triethanolamine (TEOA, 500 µL, 3.0 mmol, 80% wt in water) and the catalyst, triethylamine (TEA, 250 µL, 1.8 mmol). Increasing concentration of the catalyst increased the rate of foam formation; a near instantaneous reaction was desired [17-18]. If applicable the specially synthesized monomer, and a small amount of acetone was used to adjust viscosity. For the standard TEOA-TDI synthesis, Part B was added to Part A, for synthesis involving the special monomers, Part A was added to Part B’. The reaction took 5 seconds, increasing in temperature as it cured to form the standard polyurethane (TEOA-TDI); it exhibited significant expansion (9X) and hardening to withstand stimulation with a glass stir rod.

The exothermic cure of polyurethane foams can reach temperatures at high as 140-170 °C which result in ‘scorching’ of the polymer. Scorching weakens the urethane linkages so that they no longer withstand the mechanical stress associated with high solids loading [6]. The TEOA-TDI foam was white in color with no visible scorching (Figure 2.7). This synthetic method was altered using special energetic monomers, starting at 50:50 mole ratios, and varying until foam had a desirable structure and expansion factor.

Figure 2.7. Synthesis of (TEOA-TDI) foam
Foam of Compound 1 (TMNM(1)/TEOA-TDI)

A solution was formed (2.6 mL) from TMNM 1 (0.75 g, 5 mmol), and TEOA (1.12 g, 7.5 mmol), and 1 mL of acetone. An aliquot of this solution (500 µL) containing 1.0 mmol TMNM, and 1.5 mmol TEOA was added to TEA (250 µL, 1.8 mmol) and mixed in a 50 mL centrifuge tube; this was Part B’. Part A (the isocyanate solution) was added to Part B’; they were initially immiscible, but after swirling the mixture for about 4 seconds resulted in an increase in temperature and miscibility. At 10 seconds the reaction began to bubble, and the resulting foam expanded to 10X the original volume. This foam was yellow with no visible scorching and more crystalline in structure than the TEOA-TDI foam. It withstood stimulation with a glass stir rod (Figure 2.8).

Figure 2.8. Synthesis of (TMNM(1)/TEOA-TDI) foam assuming 1:1 mol Polyol

Foam of Compound 2 (TETRA(2)/TEOA-TDI)

A dark red stock solution (2.5 mL) was formed by adding TETRA 2 (1 g, 4.2 mmol) and TEOA (1 g, 6.7 mmol) to 500 µL acetone. Part B’ was prepared in a 50 mL centrifuge tube by adding TEA (100 µL, 1.0 mmol) to an aliquot (650 µL) of the red solution (1.0 mmol TETRA and 1.7 mmol TEOA). Part A (the TDI solution) was added to Part B’; an instantaneous reaction began; and the foam expanded 10X the original volume. The resulting foam was not stiff enough to withstand stimulation with a glass stir rod (Figure 2.9). It was easily powdered with mortar and pestle. It was dark red in color, and, despite several procedure changes, exhibited some visible scorching in the middle. Starting at 50:50 mole ratio of TETRA to TEOA, the amount of TETRA 2 was reduced
until the TETRA to TEOA ratio was 0.4. Even at this low ratio, scorching was observed in the center of the polymer mass. Lowering catalyst to 50 µL didn’t eliminate scorching.

![Figure 2.9. Synthesis of (TETRA(2)/TEOA-TDI) foam assuming 1:1 mol Polyol](image)

**Foam of Compound 3 (AZONITRO(3)/TEOA-TDI)**

One gram each of AZONITRO 3 (5.7 mmol) and TEOA (6.7 mmol) were mixed in acetone (500 µL) to form 2.5 mL of a viscous, orange solution. In a 50 mL centrifuge tube an aliquot (1 mL) of the orange solution [AZONITRO (2.2 mmol) and TEOA (2.7 mmol)] was mixed with TEA catalyst (100 µL, 1.0 mmol) to create **Part B’**. **Part A** was added to **Part B’**; in 10 seconds the reaction was complete, and the foam had expanded 9 times the original volume. This orange foam showed no scorching and could withstand stimulation with a glass stir rod (Figure 2.10).

![Figure 2.10. Synthesis of (AZONITRO(3)/TEOA-TDI) Foam assuming 1:1 mol Polyol](image)

**Foam of Compound 4 (BAMP(4)/TEOA-TDI)**

A transparent yellow solution (1.5 mL) was formed by adding BAMP 4 (1 g, 5.4 mmol) and TEOA (0.5 g, 3.4 mmol) to 500 µL of acetone. A 1 mL aliquot of this solution, containing BAMP (2.7 mmol) and TEOA (1.7 mmol) was mixed with TEA (150 µL, 1.1 mmol) in a 50 mL centrifuge tube to make up **Part B’**. **Part A** was added to **Part
B', and the foam formed and expanded 7 fold in about 6 seconds. This white foam showed no visible scorching and withstood stimulation with a glass stir rod (Figure 2.11).

![Chemical structure](image)

Figure 2.11. Synthesis of (BAMP(4)/TEOA-TDI) Foam assuming 1:1 mol Polyol

**Foam of Compound 5 (DNPD(5)/TEOA-TDI)**

Countless attempts to make a foam using as little DNPD (0.10 g, 0.6 mmol) to TEOA (0.15g, 1.0 mmol) and reducing catalyst to 50 µL resulted in a full scorching of the foam with concomitant orange fumes.

**Foams with Pyrotechnic**

To examine how significant amounts of solids loading affected polymer formation or expansion, the following experiment was performed. **Part A** was placed in a centrifuge tube and stirred. **Part B**, which consisted of TEOA and TEA, was added to **Part A**. Immediately after the reaction began, discernable by yellow coloration, and before bubbling commenced, the pyrotechnic was added, an amount equivalent to 73% solids loading. The pyrotechnic formulation was a 90/10 Ca(IO₃)₂/Al mixture, 73% solids loading is equivalent to 4.84 g pyrotechnic per 1.80g foam. The reaction mixture was stirred once before it began to expand; the reaction was complete in 20 seconds or less. The product was porous, grey in color, and exhibited similar expansion (8X) to the foam without solids.
**Scanning Electron Microscope (SEM)/ Energy Dispersive Spectroscopy (EDS)**

Pyrotechnic-loaded polyurethane foam samples were dried in a vacuum oven and transported in falcon tubes. Small slivers were cut with razor blade from the top and bottom of the expanded pyrotechnic-loaded foam. Samples were placed on the sample holder examined under low vacuum (25 Pa) in backscatter mode at a voltage of 20 kV.

**Powdered Foams with Pyrotechnic**

For calorimetry, foams were ground in a coffee grinder and sieved to particle sizes of 150-300 µm. They were mixed in a Resodyn™ Acoustic Mixer with pyrotechnic.

**Bomb Calorimetry/UV-VIS**

Bomb Calorimetry was performed using a Parr 6200 Isoperibol Bomb Calorimeter. The calorimeter was calibrated (10 trials) with benzoic acid and 2.07 MPa oxygen ($\Delta U_c = 26.4$ kJ/g). The samples were loaded and ignited in $O_2$ (2.07 MPa).

When molecular iodine ($I_2$) was produced in the bomb calorimetric experiments, it was quantified using an ultraviolet-visible (UV-Vis) spectrometer (Agilent 8453), 190 to 1100 nm, resolution 1 nm, 0.5 s integration time. Iodine was extracted from the bomb with 100 mL of an aqueous 0.5 M potassium iodide (KI) solution. The solution had excess $I^-$ which solubilized $I_2$ and transformed it to $I_3^-$ ($\lambda = 353$ nm) [19]. An example of a calibration curve for iodine quantification is shown in Figure 2.12.

![Iodine Calibration Curve](image)

**Figure 2.12. Example UV-Vis calibration curve for I$_2$ quantification**
RESULTS AND DISCUSSION

Monomers

Characterization

FTIR

In Figure 2.13, the FTIR of each monomer used is shown. At around 3200 cm\(^{-1}\) the OH stretch is visible and broad for all cases. In spectra 1, 2, 3 and 5, the stretch for NO\(_2\) are seen at 1560-1510 cm\(^{-1}\). In spectra 3 and 4, the N\(_3\) stretch is sharp at 2100 cm\(^{-1}\).

Figure 2.13. IR Spectra of TEOA (provided by NIST Chemistry WebBook), TMNM (1), TETRA (2), AZONITRO (3), BAMP (4), and DNPD (5)
In order to confirm the synthesis of the monomers, LCMS was performed. Figure 2.14 shows the results from the mass spectrometer. TETRA (2) formed a fragment [TETRA - OH] with an exact mass of 209.0415 AMU, and a chloride adduct [TETRA + Cl] with an exact mass of 275.0281 AMU. In the case of the AZONITRO compound (3), there was only one peak to verify identification, a chloride adduct [AZONITRO + Cl] with an exact mass of 211.0237 AMU. BAMP (4) formed two adducts, a chloride adduct [BAMP + Cl] with an exact mass of 211.0560 AMU, and a formate adduct [BAMO + CHO] with an exact mass of 231.0848 AMU. DNPD (5) formed a similar fragment to TETRA [DNPD - OH] with an exact mass of 135.0048 AMU, and a chloride adduct [DNPD + Cl] with an exact mass of 200.9917 AMU.

Figure 2.14. LCMS Confirmation TETRA (2), AZONITRO (3), BAMP (4), & DNPD (5)
In Figure 2.15, DSC traces of the monomers used are shown at 20 °C min$^{-1}$. TEOA, the non-energetic monomer has an endothermic decomposition at 198 °C. All the energetic synthesized monomers (1-5) have exotherms in the 200-260 °C region. The three crystalline energetic monomers show endotherms at their melting points (1, 2 and 5). The two liquid energetic monomers, (3 and 4), have only a single exotherm.

Figure 2.15. DSC Traces TEOA, TMNM (1), TETRA (2), AZONITRO (3), BAMP (4), & DNPD (5)
Polyurethane foams

Characterization

FTIR

Figure 2.16. IR Spectra of Polyurethane Foams TEOA-TDI, TMNM(1)/TEOA-TDI, TETRA(2)/TEOA-TDI, AZONITRO(3)/TEOA-TDI, & BAMP(4)/TEOA-TDI

Figure 2.17. Schematic of TEOA-TDI foam
The FTIR characteristics are shown in Figure 2.16. In Figure 2.17, for the standard foam (TEOA-TDI) the following stretches are observed: ATR $\tilde{\nu} = 3290 \text{ cm}^{-1}$ is the N-H valence vibration, $1700 \text{ cm}^{-1}$ is the valence vibration of the C=O group (amide I), $1525 \text{ cm}^{-1}$ is the amide II vibration (N-H bending), and $1220 \text{ cm}^{-1}$ is the asymmetric C-O bending vibration. Foams TMNM(1)/TEOA-TDI and TETRA(2)/TEOA-TDI, only have (NO$_2$) functionality, which literature suggests, overlaps with the C-O asymmetric vibration at around $1520 \text{ cm}^{-1}$ (can be seen anywhere between 1500-1600 cm$^{-1}$) [14]. In Figure 2.16, AZONITRO(3)/TEOA-TDI and BAMP(4)/TEOA-TDI the quintessential (N$_3$) vibration can be seen at around $2100 \text{ cm}^{-1}$.

**Thermal Properties**

**SDT**

Thermal traces of the five polyurethane foams run on TGA and DSC simultaneously show clear, two-step weight loss, the first centered around 250 °C and the second around 420 °C Figure 2.18. In the standard polyurethane, the first weight loss is endothermic, whereas in the polymers modified with the energetic monomers [TMNM(1)/TEOA-TDI, AZONITRO(3)/TEOA-TDI, and BAMP(4)/TEOA-TDI] this weight loss is exothermic. Above 350 °C, all the polyurethanes exhibit endothermic weight loss, until by 450 °C no polymer remains. These traces are interpreted as initial partial decomposition of the monomer, followed by complete pyrolysis of the organic species.
In Table 2.1, the components for the synthetic routes for each foam type are laid out along with foam characteristics—expansion factor, heat of combustion ($\Delta U_c$), and heat of decomposition ($\Delta H$). Expansion factor was calculated based on the ratio of the milliliters of liquid components, to the milliliters of the expanded foam, for example: 5 mL/45 mL = 9X (Figure 2.19). The heat of combustion, $\Delta U_c$, was experimentally determined using bomb calorimetry. Heat of decomposition, $\Delta H$, values were experimentally determined using SDT.
Table 2.1. Components of polyurethanes prepared with special monomers

| TEOA-TDI Foam | Part A | Part B |
|---------------|--------|--------|
| Composition   | mg     | mmol   | Expansion | ΔUc (kJ/g) | ΔH (J/g) |
| TDI           | 1214   | 7.0    | TEOA      | 560       | 3.0      |
| Pentane       | 313    | 4.3    | TEA       | 181.5     | 1.8      |
| mmol NCO      |        |        | mmol OH   |           |          |
|               | 13.9   |        |           | 9.0       |          |

| TMNM(1)/TEOA-TDI Foam | Part A | Part B | Expansion | ΔUc (kJ/g) | ΔH (J/g) |
|-----------------------|--------|--------|-----------|------------|----------|
| Composition           | mg     | mmol   | TEOA/TMNMM | 225/150   | 1/1.5    |
| TDI                   | 1214   | 7.0    | TEOA       | 560       |
| Pentane               | 313    | 4.3    | TEA        | 181.5     |
| mmol NCO              |        |        | mmol OH    |           |
|                       | 13.9   |        |            | 7.5        |

| TETRA(2)/TEOA-TDI Foam | Part A | Part B | Expansion | ΔUc (kJ/g) | ΔH (J/g) |
|------------------------|--------|--------|-----------|------------|----------|
| Composition            | mg     | mmol   | TEOA/TETRA | 250/250 | 1.7/1     |
| TDI                    | 1214   | 7.0    | TETRA      | 250       |
| Pentane                | 313    | 4.3    | TEA        | 72.6      |
| mmol NCO               |        |        | mmol OH    |           |
|                        | 13.9   |        |            | 9.1        |

| AZONITRO(3)/TEOA-TDI Foam | Part A | Part B | Expansion | ΔUc (kJ/g) | ΔH (J/g) |
|---------------------------|--------|--------|-----------|------------|----------|
| Composition               | mg     | mmol   | TEOA/AZONITRO | 400/400 | 2.7/2.2  |
| TDI                       | 1214   | 7.0    | AZONITRO   | 400       |
| Pentane                   | 313    | 4.3    | TEA        | 72.6      |
| mmol NCO                  |        |        | mmol OH    |           |
|                           | 13.9   |        |            | 12.5       |

| BAMP(4)/TEOA-TDI Foam     | Part A | Part B | Expansion | ΔUc (kJ/g) | ΔH (J/g) |
|---------------------------|--------|--------|-----------|------------|----------|
| Composition               | mg     | mmol   | TEOA/BAMP | 250/500   | 1.7/2.7  |
| TDI                       | 1214   | 7.0    | BAMP      | 250       |
| Pentane                   | 156.5  | 2.2    | TEA       | 108.9     |
| mmol NCO                  |        |        | mmol OH   |           |
|                           | 13.9   |        |            | 10.5       |
**Pyrotechnic Foams**

The standard foam TEOA-TDI was used to test how much pyrotechnic powder and how uniformly this powder could be introduced to the foam. The pyrotechnic mixture was added to TEOA-TDI in amounts ranging from 30 wt% to 80 wt%. It was determined that up to 73 wt% powdered pyrotechnic could be added without significantly compromising expansion (expansion was 8 fold rather than 9). To determine the uniformity of distribution of the pyrotechnic, a top and bottom sliver of the pyrotechnic-loaded TEOA-TDI foam was examined by SEM/EDS. Distribution was less uniform than desirable. The micrographs in Figure 2.20 show more pyrotechnic in the bottom slice than the top.

![Figure 2.20. SEM micrographs TEOA-TDI foam, 70% solids loading 90/10 Ca(IO₃)₂/Al EDS foam top (left)(Spot 1 Ca & I; Spot 5, Al); bottom (right)(Spot 1 Ca & I; Spot 4, Al)]
Without the presence of foam, the Ca(IO₃)₂/Al ratio which would readily burn was 75/25. With added organic, a 90/10 ratio gave optimum performance (Fig. 2.21)

Figure 2.21. Open burn of TEOA-TDI foam compared with bomb calorimetry values for molecular iodine and heat production

| Iodine production | %I₂/mix gram | Heat (kJ/g) |
|-------------------|--------------|-------------|
| FOAM              | 34           | 9.04        |
| 90/10 Ca(IO₃)₂    | 30           | 8.32        |
| 95/5 Ca(IO₃)₂     |              |             |
| +30 % FOAM        |              |             |
| 75/25 Ca(IO₃)₂    | 29           | 11.69       |
| +30 % FOAM        |              |             |

With the exception of TETRA(2)/TEOA-TDI, all the polymers shown in Table 2.1 were mixed with 70 wt% pyrotechnic mixture of 90/10 Ca(IO₃)₂/Al and the heats of combustion and iodine production determined by bomb calorimetry. TETRA(2)/TEOA-TDI was not chosen for further study because its charring suggested that mixing with a pyrotechnic might result in hazardous, unexpected ignition. To overcome the lack of uniform distribution of the pyrotechnic in the foams, for calorimetry only, the foams were powderized, and 70 wt% of the pyrotechnic (90/10 Ca(IO₃)₂/Al) was mixed in (Table 2.2). SDT of the pyrotechnic-loaded energetic and standard foams (Figure 2.22) show the pyrotechnic mixture releases heat earlier and over a longer range than without an organic matrix.
Figure 2.22 SDT of Ca(IO₃)₂/Al alone (top left) versus polyurethane foams w added pyrotechnic (90/10 Ca(IO₃)₂ + 30% foam) TEOA-TDI foam, TEOA/AZONITRO(3)-TDI foam, TEOA/BAMP(4)-TDI foam
Table 2.2. Bomb calorimetric results for pyrotechnic-loaded foams under oxygen

| Pyrotechnic-loaded Foam                                  | Heat Output (kJ/g) | std dev | % Iodine (I\textsubscript{2} formed to pyro mass) | std dev |
|----------------------------------------------------------|--------------------|---------|-----------------------------------------------|---------|
| 90/10 Ca(IO\textsubscript{3})\textsubscript{2}/Al+30% TEOA-TDI Foam | 9.04               | 0.38    | 34.0                                         | 1.84    |
| 90:10 Ca(IO\textsubscript{3})\textsubscript{2}/Al+30% TMNM(1)/TEOA-TDI Foam | 8.72               | 0.15    | 32.4                                         | 1.81    |
| 90:10 Ca(IO\textsubscript{3})\textsubscript{2}/Al+30% AZONITRO(3)/TEOA-TDI Foam | 7.52               | 0.66    | 36.7                                         | 0.80    |
| 90:10 Ca(IO\textsubscript{3})\textsubscript{2}/Al+30% BAMP(4)/TEOA-TDI Foam | 8.99               | 0.21    | 36.8                                         | 1.21    |

Within standard deviation the pyrotechnic-loaded energetic foams do not outperform the standard foam. This was not the case for the polymers when no pyrotechnic was present (Table 2.1). Apparently, the boost in energy and oxygen production provided by the pyrotechnic (70 wt% loading) overwhelms any addition boost available from the energetic monomer which makes up less than 10 wt% of the overall formulation.
CONCLUSIONS

This study sought to improve the energy output of polyurethane/pyrotechnic formulations by replacing part of the polyol TEOA with polyols containing nitro and/or azide groups. Monomers containing one or two of these functional groups were synthesized, but it was found that the presence of two nitro groups in the polyol, as in Compounds 2 and 5, resulted in a material so energetic that when combined with TDI, the polyurethane could not be produced without “scorching.” It should be noted that polyurethane resins have been made from compounds 4 and 5, but in that report polymerization was allowed to progress slowly (overnight) [14]. In contrast, the diazo group, one nitro group, and one azo/one nitro were successfully inserted into a polyurethane. We believe TMNM 1 and AZONITRO 3 polyurethanes are reported here for the first time.

It was found that a pyrotechnic powder could be mixed with the polyurethane foams at levels up 73% solids with little negative impact on the foam expansion; it was only reduced from 9 to 8 fold. Furthermore, the pyrotechnic added could contain less aluminum since fuel was supplied by the polyurethane. Whereas at least 25% aluminum was required to produce ignition in a Ca(IO₃)₂ powder, in the presence any of the polyurethane foams the oxidizer/aluminum ratio could be raised to 90/10 and still be readily ignited. Reduction of aluminum resulted in increased output of molecular iodine.
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