Supplemental Information

**Improved Explosive Collection and Detection
with Rationally Assembled Surface Sampling Materials**

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The supplemental information that follows contains details about the experiment, the results, and a discussion which 5 pages long and contains 3 Tables and 3 Figures.

Experimental

Surface Pretreatment

Pretreatment of the FGC for surface modification was necessary for commercial fiber coating and to prepare the glass surface for chemical modification. Typical pretreatment of thick glassfibers was accomplished by treating in acetone for 3 h, followed by 1.0 M NaOH for 4 h, cleaned with water, and the excess NaOH then was eliminated by neutralizing with 0.1 M HCl for 30 min. Thin FGC was treated in the same fashion as the thick one, but with a reduction in of dipping time in NaOH solution from 4 h to 1 h. A dipping time of 1 h in 2.0 M NaOH, and 30 min in 0.2 M HCl was also used for thin Astroquartz® fiberglass.

Instrumentation and Analysis

A Barringer Ionscan® 400A ion mobility spectrometer (Smiths Detection) was used in this study. This IMS is designed to be used with muslin cloth wipes (or other compatible wipes) via a sliding stage mount. A thermal desorber is used to volatilize explosive compounds localized on the wiping material, and a sample carrier gas directs the compounds to a glass inlet liner that ends at an ionizing source. The ^{63}Ni β source ionizes air producing O_2^- and the addition of a chlorinated hydrocarbon dopant produces Cl^- ions that are used in the chemical ionization of the explosive vapors. These ions are then carried by an electric field to a collector.[59] The drift time (or mobility), adjusted by using an internal calibrant, was used to identify the explosive compound. The instrument was operated in negative ion mode at a desorber temperature of 180°C (unless stated otherwise) and a collection time of 10 s. The drift and inlet temperatures were set at 114°C and 240°C, respectively. The sample gas was set at 239 mL/min and the drift gas at 351 mL/min.

Sample analysis consisted of first mounting an un-deposited wipe on the stage and passing it through the IMS to obtain a background spectrum. The wipe was then deposited with 1 µL of a 10 ng/µL TNT in methanol solution using a 2 µL GC syringe. Approximately 15-20 s were allowed for the solvent to vaporize, leaving the explosive residue. The deposited wipe is passed through the IMS one minute after completion of the baseline run for consistency (*i.e.*, 1 min process time), unless otherwise noted. All comparable data was collected at the same time to avoid IMS instrument variations with time and conditions.

The ion mobility spectra were analyzed to determine the maximum TNT signal and noise. The TNT peak utilized had a reduced mobility (K_o) of 1.45 $cm^2V^{-1}s^{-1}$ and was in agreement with values reported in literatures (Harvey et al., 2009; Koyunch et al., 2005). In certain cases a background subtraction was performed by subtracting the background signal (at TNT K_o) from the TNT signal of the deposited pass. Noise was calculated by taking the root mean square (RMS) along the 16 ms drift region.

Throughout most of this work the data is present as values normalized to the response of muslin. Normalized IMS signal responses were presented to provide an easily comparable response between sampling materials, and an instrument independent value. All values normalized to 0.32 mm thick muslin unless otherwise noted.

(1) S. Harvey, R. Ewing, M. Waltman, *Int. J. Ion Mobility Spectrom.* 2009, **12**, 115-121.
(2) H. Koyuncu, E. Seven, A. Çalimli, *Turk. J. Chem.* 2005, **29**, 255-264.

Sampling Cloth Characterization

Swipe material thickness measurements were obtained using a Mitutoyo Absolute Digimatic Caliper Series 500 (Aurora, IL) by taking ten measurement points from five different pieces of each respective swipe (minimum 50 points). The error reported was the standard deviation of all measurement points. Density measurements were obtained by taking the mass of swipes and dividing by the known dimensions. Values reported as averages of five density measurements.

Surface area measurements were taken using a Quantachrome Autosorb iQ-Chemi gas sorption analyzer (Boynton Beach, FL). Swipe materials were cut into small pieces and vacuum dried at 180˚C overnight using the built-in degas station. Krypton (ultrapure, fill in details, etc.) gas was used as the sorption gas. The surface area was determined using a multi-point BET calculation.

Table SI 1. Data for Physical Discussion

Material	Thermal Conductivity (W/m-K)	Specific heat capacity (J/g-°C)
Cellulose[A]	0.242	1.338
Cotton[B]	0.071	1.335
Silica[C]	1.3	0.937
E-glass Fiber[D]	1.28-1.32	0.78-0.82, 0.803[E]
S-glass Fiber[D]	1.44-1.46	0.72-0.75, 0.736[E]
polyamide polymers[F]	0.23-0.29	1.26-1.7
Polytetrafluoroethylene[F]	0.25	1.0

A. Curtis, L.J., Miller, D.J., Transport Model with Radiative Heat Transfer for Rapid Cellulose Pyrolysis. Ind. Eng. Chem. Res., 1988,27, 1783-1788
B. Harris, M., *Harris's Handbook of Textile Fibers*, Harris Res. Lab., Inc., Washington, D.C., 1954.
C. http://www.tekna.com/powder/spherical-powder/silica.html
D. JPS Composite Materials databook. http://jpsglass.com/
E. Lubin, G. Handbook of fiberglass and advanced plastics composites, Robert E. Krieger Pub. Co.: Huntington, N.Y, 1969.
F. Martienssen, W. and Warliment, H (Eds). Springer Handbook of Condensed Matter and Material data, Spinger Berlin Heidelberg.: Germany, 2005.

Table SI 2. Additional Physical Data on Unmodified Sampling Materials

Material[2]	Trade Name Designator	Thickness (mm)	Surface Area (m^2/g)
Muslin	-	0.26	1.04
Organic Coated FGC	Greige	0.26	0.40
Unfinished FGC	537A	0.24	0.38
Pure silica FGC silane finished (PSiSF)	Astroquartz®	0.29	0.22
Polymer Primer (PP) E FGC	497A	0.27	0.40
Polymer Primer (PP) S FGC	497A	0.26	0.31
Cl Silane FGC E glass	CS724	0.23	0.53
Cl Silane FGC S glass	CS724	0.28	0.61
PTFE FGC	Teflon	0.20	0.58
Activated carbon cloth	Zorflex®	0.77	880

Table SI 3. Normalized IMS Response to TNT from Pure Silica Fiberglass Cloth

Material[1]	TNT Normalized Signal[2] (10ng)	TNT Normalized Signal[2] (5ng)
Muslin	1.0 ± 0.1	0.4 ± 0.3
PSiSF FGC	4.5 ± 0.3	2.4 ± 0.4
Phenyl on PSiSF FGC	10.5 ± 0.2	7.3 ± 0.2
BF- Phenyl on PSiSF FGC	9.9 ± 0.4	8.3 ± 0.2
BF- Phenyl on Thin PSiSF FGC	10.0 ± 0.3	8.6 ± 0.2

1. PSiS FCG – pure silica silane finish cloth
   FGC – fiberglass cloth
   Standard thickness 0.26 mm, thin material 0.10mm thick
   Additional data on pure silica FGC available in Table SI 3.
2. Materials preconditioned at 180°C overnight under vacuum. Response to 10 ng liquid TNT deposition.

The phenyl silane surface functionalization of the pure silica fiberglass material (PSiSF) clearly impacts its performance as a sampling material. Both TNT deposition amounts on the Phenyl on PSiSF surface show a large increase in the relative IMS signal response compared with as-received PSiSF. However, a second functionalization step and a reduction in thickness

did not significantly enhance the performance, likely due to saturation (at the 10 ng level) as well as near quantitative analyte release (at the 5 ng level). The single stage phenyl functionalization on the pure silica surface provided a significantly higher relative TNT signal than E or S glass. This is likely due to the fact that pure silica contains a higher density surface silanol sites which increases density of organosilane layers that can be installed beyond that of E or S glass. Unfortunately, while the pure silica is simpler, cleaner, and ultimately provides slightly better analyte recovery, it is also significantly more expensive and the brittle fibers fracture easily making the material physically much less durable (particularly for the thinner material).
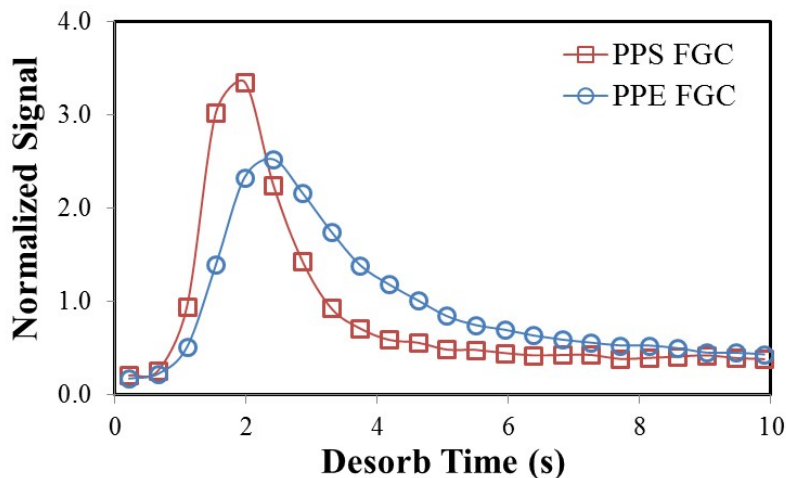

Figure SI 1. Normalized IMS desorption profile for E and S FGCs materials (using a base of polymer primary/497A finish). Signals normalized to muslin deposited using a 10ng TNT solution. The better thermal conductivity and reduce specific heat of S glass clearly shows the advantages of S glass over E glass.
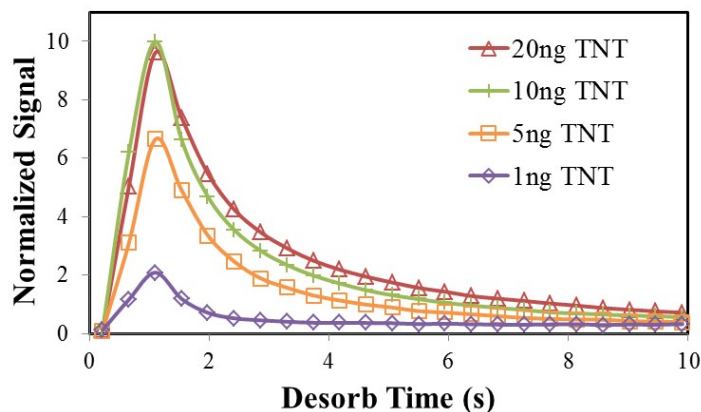

Figure SI 2. Normalized IMS desorption profile for thin BF- Phenyl S FGC sampling material with various TNT deposition. Area under the curve is proportional to the amount of TNT detected until instrument saturation is reached (~10 ng TNT for this particular material). At TNT concentrations above 10 ng the area is not proportionally representative of TNT detected.
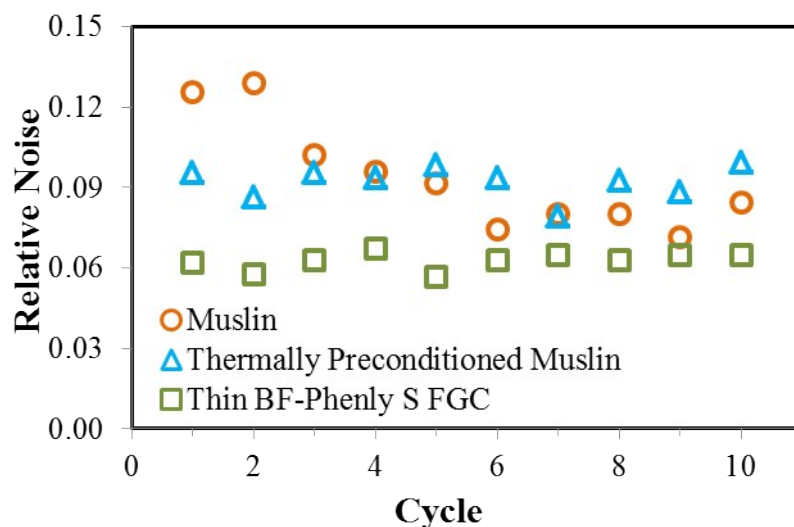
Figure SI 3. Relative IMS noise using 10 ng TNT solution deposited on muslin and BF- Phenyl on thin S FGC. The detection was repeated a total of 10 times on the same piece of respective material. Thermal conditioning of muslin reduced the noise and stabilizes it to a uniform level near that of functionalized fiberglass than has been thermally preconditioned. Noise was calculated by taking the RMS at a 16 ms drift time.

The noise level was not observed to change for thermally preconditioned muslin but the relative signal change for untreated (as provided) muslin notably decreased with each consecutive cycle until a baseline is reached after approximately six cycle. This suggests that active surface sites and impurities on the muslin are being sequentially reduced with each thermal cycle. This conjecture is supported by similar trends observed in the background noise from the swipe materials.