Rapid Spatial Mapping of Chemicals Dispersed Across Surfaces using an Autosampler /DART/TOFMS

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Introduction. Accidental, deliberate, or weather-related dispersive events can spread chemicals onto surfaces over a large area. First responders must rapidly determine the dispersal direction, distance, and the identities of the chemicals. A compass-based sampling scheme is illustrated in Figure 1. Direct Analysis in Real Time/Time-of-Flight Mass Spectrometry (DART/TOFMS) mass-analyzes absorbates on cotton-swab, wipe samples in 6 seconds per swab using a simple and inexpensive autosampler based on N-scale model railroad flat cars and track. Exact masses of precursor and product ions accurate to within 2 mmu yield tentative identifications, even when a compound is not found in an exact-mass library.

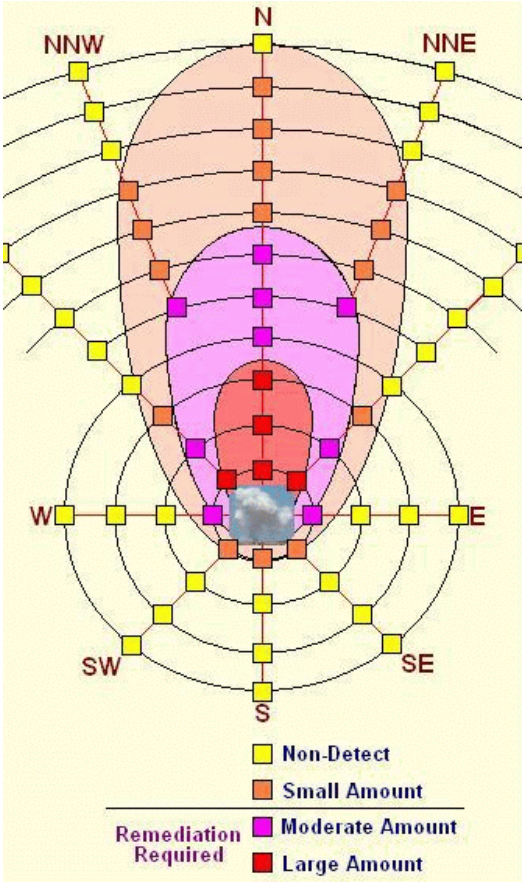

Figure 1. Simulated chemical dispersion pattern with a compass-based sampling scheme.

Hundreds of samples must be analyzed rapidly to guide remediation efforts and to document meeting targeted levels. Figure 2 illustrates a sampling scheme with 1,000 grid points. Such large sample sets could also be used to thoroughly characterize Superfund sites, wherein small "hot spots" of contamination could be revealed.

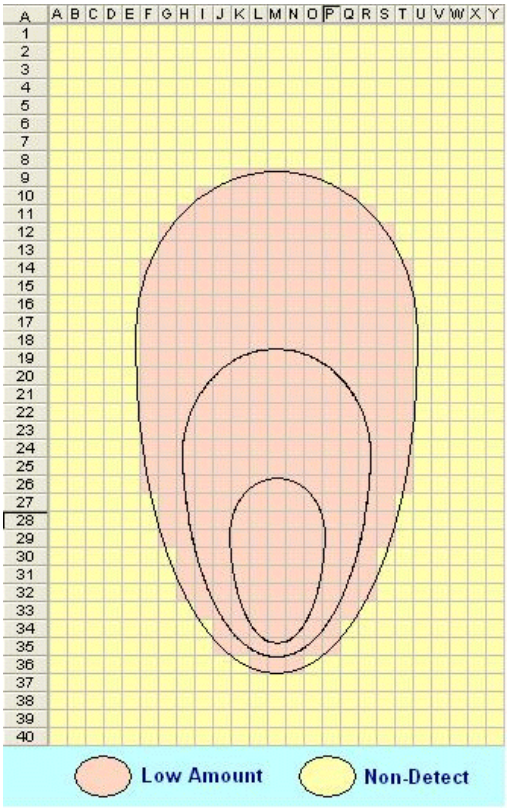

Figure 2. Simulated chemical dispersion pattern after successful remediation. A 25 x 40 grid would provide 1,000 sampling points.

Methods. *Autosampler.* To achieve our goal of having one analyst receive, prepare, analyze, and provide dispersion maps for 1,000 wipe sample analyses in one 8-hour shift, ruggedness and simplicity are mandatory. Figure 3 shows the DART open-air, ionization region with cotton swabs mounted through a 3-foot-long, ½-inch square aluminum bar. The bar is supported by two N-scale model railroad flat cars and is pulled through the DART at a steady speed by a small, 7-rpm motor in 7.5 min.

The two towers and four pulleys in Figure 4 provide in excess of 3 feet of travel for the bar during which all 76 cotton swabs are exposed sequentially to the heated beam of metastable helium atoms. The beam desorbs and ionizes analytes on each swab. The ions are pulled into the mass spectrometer to produce full scan mass spectra that are recorded within a single data file for the 72 analyte and four calibrant swabs.

Wipe Sample Transport. Receipt of 1,000 individually double-bagged, 6-inch-long, cotton-swab, wipe samples would require more than one shift to open the bags, insert the swabs into bars, and truncate the sticks. To simplify wipe sample collection and to provide them to the analyst in a nearly ready-to-analyze state, the wipe sample transport in Figure 5 was built. The support bar is the core

element. Encasing each swab is a 1.8-mL vial that protects the swab before and after a sample is collected. The vials are held in place by a linear cell array fashioned inexpensively from manila folders and packaging tape. The field sampler pushes up on a stick, removes the vial from the swab, collects the wipe sample, covers the swab with the vial, reinserts the swab and vial, and snips off the stick at the base of the cell assembly. Truncating the stick prevents use of a swab for multiple wipe samples and readies the swab for analysis.

In Figure 6a, the bar-vial-cell assembly has been removed from the wipe sample transport and precut slits covered with packaging tape are being cut with a hobby knife. After the bottom of the cell array falls, the remainder of the array is lifted upward (Figure 6b). After inserting four calibrant swabs, the bar and swabs are ready for the autosampler.

In Figure 7, 14 bar-vial-cell assemblies supporting 1,000 protected cotton swabs are shown in a portable carrier.

Preliminary Data. *Ionizing Beam Diameter.* The ionizing beam must have a diameter less than the distance between the swabs to avoid interference from adjacent swabs. This diameter was estimated from ion chromatograms obtained for sets of 11 melting point tubes (MPTs) that had been dipped into an analyte solution and dried before being inserted into holes in an aluminum bar. As illustrated in Figure 8a, each MPT was separated from the next by increasing distances of 1/32", 1/16", 3/32", ... 5/16". The holes were drilled off-center along the bar axis to test for ionizing beam dispersion over a distance of 5/32" by passing the support bar through the ion source with the holes closer to the cone orifice or to the ionizing beam origin. In both cases, the baseline was first reached between the third and fourth MPTs in Figure 8b, which were 3/32" (2 mm) apart, indicating minimal, if any, dispersion. This was the smallest distance that allowed the ionizing beam to pass cleanly between the two MPTs and was less than the distance between cotton swabs in Figure 3.

Figure 3. Ionization region of the DART through which an aluminum bar supporting cotton swabs is pulled. Two alignment devices determine the position of the swabs within the ionizing beam.

Figure 4. The autosampler/DART/TOFMS.

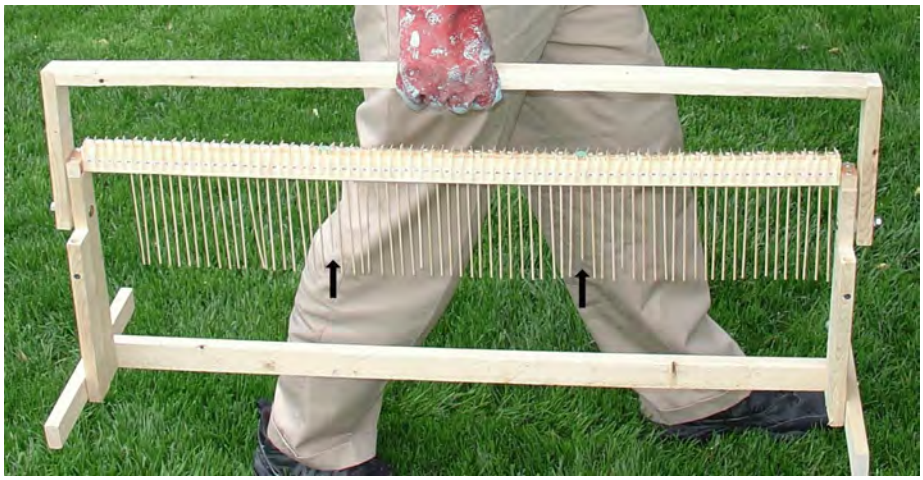

Figure 5. The wipe sample transport comprised the support bar, 6-inch cotton swabs, 1.8-mL glass vials, linear cell array, and pine stick carrier. The arrows locate two spare swabs where calibrant swabs will be placed prior to analysis.

Relative Standard Deviation. Seventy-two cotton swabs were dipped into a solution of 2-aminobiphenyl for 10 s and allowed to dry. Four swabs were dipped into a PEG 200 calibrant solution and dried. The m/z 170 ion chromatogram for the precursor ion is shown in Figure 9a. As depicted in Figures 9b and 9c, two chromatographic peaks were observed for each swab as the ionizing beam grazed the leading and trailing edges of each one. Each peak was delineated by at least four 0.1 s scans. Five sets of swabs dipped into solutions of one of three analytes provided %RSDs (N=72) of between 18.5% to 21.3% and maximum/minimum ratios for the paired chromatographic peak areas from each swab of between 2.2 and 2.7. These results suggest that semi-quantitation into low, moderate, and high concentrations differing by factors of 10 or more might be feasible for cotton-swab, wipe samples.

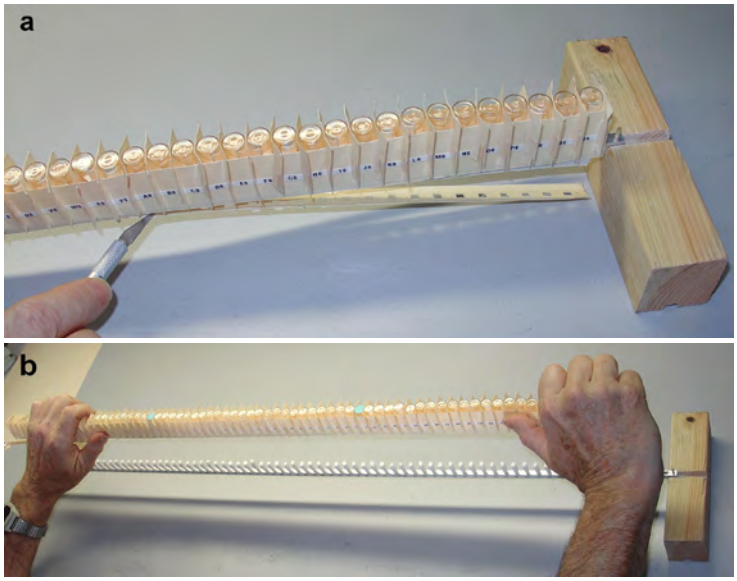

Figure 6. (a) Cutting off the bottom portion of the cell array and (b) lifting the remainder of the array upward to reveal the cottons swabs.

Exact Mass Accuracy. Baseline abundance was observed for the four swabs dipped into PEG 200 in Figure 9a. All analyte mass spectra from 72 swabs were recorded within 1.3 min of the last or next recorded calibration mass spectrum to minimize calibration drift. All 72 exact masses were correct within 1 mmu and nearly all to within 0.5 mmu. This observation suggests that if the instrument were fielded in a van parked near a Superfund or dispersal site on a partially cloudy day, calibration drift over 1.3 min intervals due to temperature changes would be minimal.

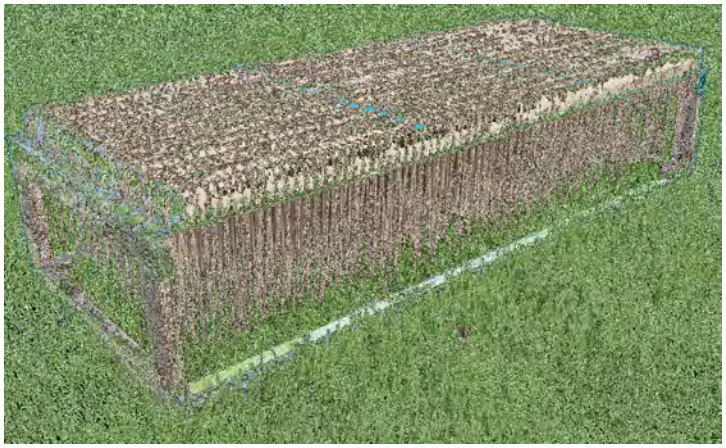

Figure 7. 1,000 cotton swabs ready for deployment.

Conclusions and Future Work.

◆ An inexpensive autosampler for an open-air ion source has been built, tested, and an optimal sample speed has been determined.

◆ Maximum/minimum ion abundance ratios of 2.2-2.7 from five sets of 72 analyte swabs suggest semi-quantitation is feasible.

◆ A wipe sample transport has been built to simplify field sampling and to provide wipe samples nearly ready to analyze.

♦ Sub-groups of the 1,000 cotton swabs will be dipped into low, moderate, or high concentrations of an analyte to test the anticipated 1,000 samples/day capability and the rapid preparation of a dispersion map.

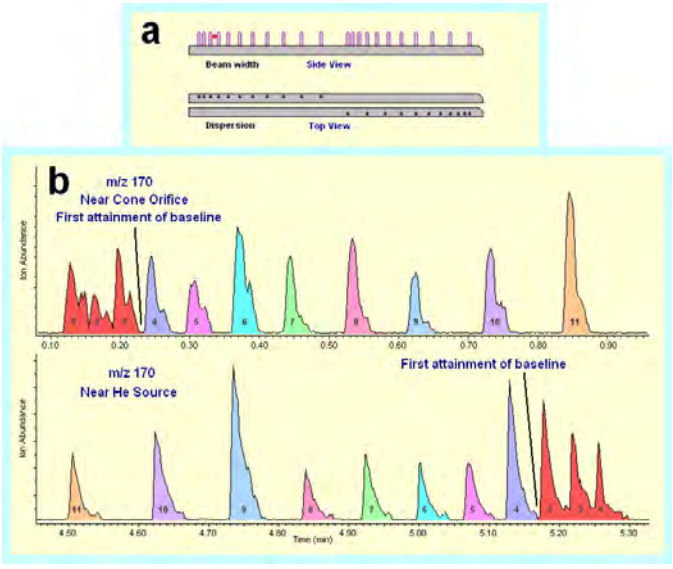

Figure 8. (a) Hole locations in an aluminum bar to support melting point tubes and (b) m/z 170 ion chromatograms for both directions of bar travel.

♦ A small-scale dispersive event will be conducted (<100 swabs) using innocuous compounds to investigate the practicality of collecting actual wipe samples.

♦ Detection limits for several compounds based on wipe sampling will be determined.

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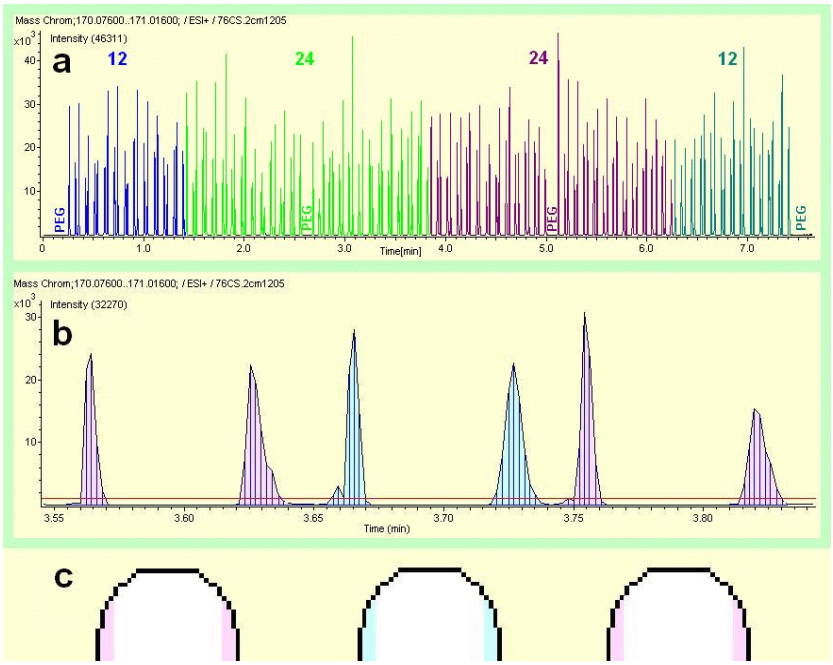

Figure 9. (a) An m/z 170 ion chromatogram for 76 cotton swabs with a bar speed of 0.20 cm/s and scan rate of 10 spectra/s. (b) A magnified portion of the ion chromatogram. The red line is drawn at 20 times the average baseline amplitude, which is used to determine when chromatographic peaks begin and end. (c) The locations of the three swabs relative to the observed ion abundances.