

Rapid Semi-Quantitative Surface Mapping of Airborne-Dispersed Chemicals using Mass Spectrometry

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Abstract

Chemicals are dispersed accidentally, deliberately, or by weather-related events. Rapid mapping of contaminant distributions is necessary to assess exposure risks, to plan remediation, and often to determine the source of dispersed chemicals. Powdered aspirin or caffeine was dispersed across a concrete driveway using the exhaust port of a shop vacuum cleaner. Water-soaked, cotton-swab, wipe samples were collected to map the dispersant distribution. An autosampler/Direct Analysis in Real Time (DARTTM)/time-of-flight mass spectrometer was used to acquire an ion chromatogram for the most abundant ion. A semi-quantitation map for several levels of caffeine was plotted to demonstrate the feasibility of applying this technology to contaminated sites.

Introduction

Mapping a contaminated site semi-quantitatively into high, moderate, low, and non-detect levels would aid in assessing risks posed by the site to humans and the environment, in planning thorough remediation, and in identifying or confirming sources of dispersed chemicals.

Assuming adequate sample density, four requirements must be met to provide rapid analyses for semi-quantitatively delineating with high spatial resolution the distribution of chemicals resulting

from deliberate, accidental, or weather-related dispersion of chemicals:

- Samples must require little or no preparation prior to analysis,
- Samples must be analyzed in seconds,
- Samples must be analyzed sequentially after a short intra-sample time, and
- Software to rapidly plot semi-quantitation maps must be written.

An inexpensive autosampler that provides mass-spectral analyses of 76 cotton-swab wipe samples in 7.5 min was built previously (Grange, 2008a, 2008b) to provide rapid analysis with a short intra-sample time. The cotton-swab wipe samples were pulled through the flow of hot, energized helium from a Direct Analysis in Real Time (DARTTM) ion source. Operation of the DART is simple relative to ambient-air sources that require adjustment of numerous variables and continuous delivery of solutions to the ionization region during analyses (Takáts et al., 2005). To limit sample preparation, a field sample carrier was built to simplify wipe sample collection and label bookkeeping and to provide the swabs to the laboratory nearly ready for analysis (Grange, 2008c). The macro procedures required to rapidly plot multi-color, semi-quantitation maps based on individual ion chromatograms obtained for sets of swabs is briefly described herein. To investigate the feasibility of semi-quantitation using cotton-swab wipe samples, a small-scale, dispersive event was simulated by expelling powdered NoDozTM (caffeine) tablets upon a driveway with a shop vacuum cleaner operated as a blower.

Experimental

DART/oa-TOFMS

The DART ion source directed a gas stream of metastable helium atoms nominally heated to

300°C at the cotton swabs. Analyte was desorbed, ionized by a process similar to atmospheric pressure chemical ionization (APCI)(Cody, 2005), and mass analyzed after being pulled through a cone orifice into a JEOL AccuTOFTM orthogonal-acceleration, Time-of-Flight Mass Spectrometer (oa-TOFMS) (JEOL USA, Inc., Peabody, MA). Researchers have detected numerous compounds (Williams et al., 2006; Vail et al., 2007; JEOL, 2008) using this instrument, including chemical warfare agents (Laramée et al., 2008).

Instrument Parameters

Only the positive-ion mode was used. Instrument parameters were chosen based on manufacturer recommendations, tuning the instrument for high resolution and high ion abundance, and limited observation of the effect of ranges of variables on ion abundances. The instrument settings were: ring lens: 5 V; orifice 1: 15, 20, 30, or 40 V; orifice 2: 5 V; cone temperature: 120°C; peaks voltage: 600 V; bias: 28 V; pusher bias: -0.50 V; focus voltage: -120 V; focus lens: -5 V; quadrupole lens: 7 V; right/left: -15 V; top/bottom: -2 V; reflectron: 800 V; pusher voltage: 778 V; pulling voltage: -778 V; suppress voltage: 0.20 V; flight tube: -7.0 kV; detector: 2.3 kV, He temperature: 300°C; and spectrum accumulation time: 0.97 s. The He flow was set to 2.6 L/min to minimize the risk of particles being blown off swabs and plugging orifice 1. The resolving power was 4400 and 5500 (FWHM) at m/z 121 and 195, respectively.

Autosampler

The autosampler seen in Figure 1 consisted of a 3-ft-long, ¼-in-square aluminum bar with 76 holes to support cotton swab heads mounted on two N-scale model railroad flatcars that were

pulled along N-scale track (Bachmann Industries, Philadelphia, PA) by a nylon, monofilament fish line. Up to 6 ft of travel for the bar was provided by 6-ft wooden posts on each end of the horizontal track support. Two pairs of pulleys provided direction changes for the fish line. Weights (bolts) on each end of the fish line kept the line taut about the drive wheel on the shaft of a 7-rpm DC motor powered by a model railroad transformer, which provided a variable speed. The speed was usually set to 0.2 cm/sec for the cotton swabs as they traversed the ionizing gas stream. Additional autosampler details are provided by Grange (2008a and 2008b). Unlike the commercially available autosampler for a DART ion source (IonSense, 2008), the autosampler in Figure 1 allowed use of cotton-swab wipe samples and provided a short intra-sample time (~3 s between swab edges) for sets of up to 76 swabs.

Field Sample Carrier

The core element of the field sample carrier in Figure 2 was the 3-ft-long support bar for the swabs. A linear cell array made from manila folders and packaging tape held inverted, wide-mouth, 1.8-mL glass vials in place that protected the swab heads from contamination before and after wipe samples were collected. The swab sticks were clipped off at the base of the cell assembly to avoid using a swab for multiple wipe samples and to ready the swabs for analysis. Vial and cell array removal required only a few minutes. Field sample carrier details are provided in by Grange (2008c).

pH Measurement

pH paper (Panpeha, Sigma-Aldrich, St. Louis, MO) was used to estimate the pH of water and of

water to which concentrated HCl (A.C.S.Certified Plus, Fisher Scientific, Fair Lawn, NJ) or NaOH (Food Grade, J. T. Baker, Phillipsburg, NJ) was added.

Standards

The 2-aminobiphenyl (99+%) and caffeine (99%) on-hand were previously purchased from Aldrich (Milwaukee, WI). Aspirin tablets (325 mg) were purchased from Costco, Inc. (Issaquah, WA), and NoDoz tablets (Novartis Consumer Health Inc, Parsippany, NH) were purchased from a supermarket.

Cotton Swabs

Two sizes of glueless cotton swabs with wood sticks (Puritan Medical Products, Guilford, ME) were used. The sticks were 6-in long and the cotton head diameters were about 0.26 in or 0.20 in. By visual comparison, the larger diameter heads contained about twice as much cotton.

Methodology, Results, and Discussion

Wipe Sampling Techniques

Direct analysis of surfaces collected from the field would provide greater sensitivity than any wipe sample (Laramée et al., 2008), but could require considerable effort for collection and leave damaged surfaces behind, such as holes in cement or plaster surfaces that were not contaminated. For dispersive events, a large amount of the dispersed compounds will provide sufficient material for their detection using wipe samples. Gauze pads are more commonly used to acquire wipe samples than cotton swabs (ASTM International, 2006; U.S. Environmental

Protection Agency [USEPA], 2007). However, Q-tips[®] provided a higher recovery than cotton cloth for distilled mustard from painted surfaces and similar recoveries for distilled mustard and sarin from concrete in a Norwegian study (Opstad et al., 1999). Wet swabs provided higher recoveries than dry swabs. In our study, wet-cotton-swab wipe samples were acquired to take advantage of the high throughput afforded by the autosampler and field sample carrier. An area 10 x 10 cm was delineated by fish line or a template as described below. Each cotton swab was dipped into a solvent and rolled back and forth across the area from left to right such that all of the area was contacted. The swab was rotated 90° and the rolling was repeated in the orthogonal directions. This sampling technique tended to spread out small specks of analyte throughout the area and to provide a more uniform level of the analyte around the circumference of the swab. Because only analyte from the leading and trailing edges of the swab is desorbed, ionized, and mass analyzed, a uniform distribution around the swab should provide lower RSDs. Rubbing the swab without rotation across rough surfaces such as concrete would wear away cotton and fail to distribute the analyte around the swab.

Mirror Test Surface

For solvent selection and dynamic range tests, a 36- x 30- x ¼-in, polished-edge mirror was placed on a sheet of ¼-in-thick fiberboard that provided a 1-in margin around the mirror. Holes were drilled and tapped (6-32) into the fiberboard to accept screws spaced alternatively 2 cm and 10 cm apart on all four sides and ½-in from the mirror edges. Fish line was tied to one screw and then treaded around the screws to provide a grid of 42 squares, 10 x 10 cm, separated from each other on all sides by 2 cm.

Driveway Grid Delineation

Because marking grids using pegs and fish line is impractical in the field, especially on rugged terrain or paved surfaces, a 10- x 10-cm template was constructed for simulated dispersion events. An 18-cm square frame was made from a larger cardboard frame normally used to support a transparency for overhead projection. An unexposed transparency was wiped free of film using methanol and taped over the frame. A 10- x 10-cm square was then cut from the center using a hobby knife. The frame sides were 2.5-cm wide and a 1.5-cm border of clear transparency surrounded the 10-cm-square sampling area. The non-absorbant transparency border was wiped clean with water-soaked and dry tissues between wipe samples.

Figure 3 illustrates how the grid was delineated after 10 NoDoz tablets pulverized in a mortar and pestle and placed in the back end of an 18-in-long, 1-in-inner diameter tube from the shop vacuum were dispersed. The driveway was hosed off with water and allowed to dry before the dispersion to minimize pick up of debris from a nearby pine tree. To start, the template was placed just in front of the origin of the expelled analyte at position D1 to ensure that the grid would be centered relative to the origin, and marks were made through the holes. The template was held in place by masking tape while a sample was collected. Then the template was moved to the left so that the two right holes aligned with the marks from the two left holes made previously. To skip a column, thereby doubling the width of the grid, marks were made through the left holes, the template was again moved to the left, two marks were again made through the left holes, and sample C1 was collected. This process was repeated to collect the samples from the B1 and A1 positions. This sequence was repeated starting with the D1 reference marks for

positions E1, F1, and G1 making marks through the right holes of the template to complete sampling of row 1.

After wipe samples were collected for each row, the template was moved away from the origin one position by aligning the bottom holes with the top marks made with the template at position A#. Then marks were made through the top holes. The template was moved similarly a second time and marks were again made through the top holes before samples were collected. For rows 2–12, the sampling sequence was A#, B#, ...G# to conform with the order of the swab labels on the cell assembly and aluminum bar thereby avoiding possible confusion regarding sample locations. The decision to skip both rows and columns was made after observing the travel of the cloud of caffeine powder. Sampling a larger area was more likely to map most of the deposited analyte. All 84 wipe samples were collected between dawn and noon.

Solvent Selection

Organic solvents and water were observed to affect the appearance of the swabs differently. To characterize the effects, the grid-delineated mirror described earlier was used. The mirror provided a smooth, non-porous surface for determining RSDs for cotton swabs that result from wipe sampling from a smooth, non-absorbant surface.

Blank wipe samples were taken from the mirror using the three swabs in Figure 4a. From left to right the swabs were first dipped into methanol (Burdick and Jackson, High Purity Solvent, Muskegon, MI), 91:9 isopropanol:water (IPA), or distilled water from a supermarket. Unlike the swabs dipped into the organic solvents, the water-dipped swab was compacted and

cotton fibers extending away from the body of the swab were not observed.

To determine the influences of cotton fiber compaction on the RSDs of acquired data, a small volume (300 μ L) of 2-aminobiphenyl solution (100 mg in 100 mL of methanol) was deposited in the center of each of 14 mirror squares and allowed to dry before wipe samples were taken. The solution covered about half of the area in each square before the solvent evaporated.

In Figure 5 ion chromatograms for m/z $170.0964 \pm$ (plus or minus) 0.050 Da (the calculated mass for the $[M+H]^+$ ion from 2-aminobiphenyl) acquired with an orifice 1 voltage of 15 V are shown for sets of seven swabs dipped into isopropanol or water acidified to a pH of 2. The ion abundance is zero when the ionizing gas is blocked by the swab. The blockages lasted longer for the wider swab heads that had been dipped into isopropanol. Because the compacted swab heads dipped into pH 2 water provided a longer time between the swab edges of adjacent swabs, the baseline between swabs more closely approached zero.

The areas of the pair of chromatographic peaks from each swab were calculated by setting a threshold to define the onset and end of each peak. The threshold was 55 and 11 times the average noise level for the isopropanol- and water-dipped swabs, respectively. The average noise from room air was taken as the average of the first 10 points. The data for both sets of swabs were recorded during the same data acquisition. The %RSDs (N=7) were 18.2 and 14.5, and the maximum/minimum paired area ratios were 1.74 and 1.41 for the isopropanol- and water-dipped swabs, respectively. The average paired areas for water were 24% greater than for the isopropanol-dipped swabs.

Water was chosen as the best solvent for additional experiments due to the compaction

of swab heads, which provided smaller diameter heads, longer intra-swab times, and the absence of extended fibers, which could plug the orifice into the mass spectrometer. If an analyte of interest is not well recovered using water, an organic solvent could be used instead. If a compound is easily hydrolyzed, an ion from a hydrolysis product could become the semi-quantitation ion.

Test Analytes

Aspirin and NoDoz tablets were investigated for their suitability for dispersion due to their ease of purchase, low cost, and low toxicity. Initially, to provide elemental compositions of the ions in the full scan mass spectra and to choose an appropriate semi-quantitation ion, collisionally induced dissociation (CID) voltages of 15, 40, and 70 V were applied sequentially to orifice 1 during a single data acquisition. Aspirin or caffeine was rubbed onto wet swabs in amounts sufficient to provide clean mass spectra at the three CID voltages. For aspirin, the $[M+H]^+$ ion was not observed, as illustrated by Figure 6a, but a prominent $C_7H_5O_2^+$ ion at m/z 121 was observed. Text files of the m/z ratios and corresponding mass peak areas for the spectra were prepared by the data system and imported into in-house, ion correlation software that automatically determined the compositions of the ions (Grange and Sovocool, 2008).

The average weights of three aspirin and three NoDoz tablets were 376 mg and 445 mg, respectively. The doses of 325 mg of aspirin and 200 mg of caffeine were 86.4% and 44.9% of the tablet weights. Despite the presence of additives, the $C_7H_5O_2^+$ ion from aspirin (calculated m/z of 121.0284) and the caffeine $[M+H]^+$ ion ($C_8H_{11}N_4O_2^+$, calculated m/z of 195.0876) dominated the mass spectra in Figure 6.

Semi-Quantitation Ions

The relative abundances of the m/z 121 ion from aspirin with orifice 1 voltages of 15, 40, and 70 V were 0.05:1:0.21, respectively, when swabs were dipped into a 100 mg/100 mL solution of crushed aspirin tablets in methanol. Hence, the m/z 121 ion and an orifice 1 voltage of 40 V were chosen for semi-quantitation. Because aspirin decomposes at its boiling point of 138–140°C (Chemical Safety Data, 2005), the m/z 121 ion could result from decomposition followed by ionization and/or CID of the precursor ion.

Spectra were obtained for swabs dipped into a suspension of 111 mg NoDoz/100 mL methanol (50 mg caffeine) using orifice 1 voltages of 15 through 50 V in 5 V increments. The largest m/z 195 abundance was found using 30 V, and this voltage was used for semi-quantitation of caffeine.

Choice of pH

Figure 7 is a 121.0284 ± 0.050 Da ion chromatogram from a single data acquisition showing the relative heights of the ion abundances observed when sets of seven cotton swabs dipped into water with three different pHs were used to collect aspirin wipe samples from the mirror. The average paired chromatographic peak areas decreased in the proportions of 100:38:3 for pHs of 2, 7, and 12, respectively. The %RSDs (N=7) were 24.1, 24.1, and 19.0, and the maximum/minimum ratio of areas for the paired chromatographic peaks for each swab were 2.00, 2.03, and 1.90 for pHs of 2, 7, and 12, respectively. Two factors may account for the low ion abundance for a pH of 12. Aspirin decomposes in alkali hydroxide solutions (Merck & Co.,

1989) and the sodium salt of aspirin would be less volatile than the neutral molecule and hydrochloride.

Seven-swab sets were collected using swabs dipped into water with the same three pHs for the 111 mg NoDoz/100 mL methanol suspension (50 mg of caffeine). The proportions for the average paired chromatographic peak areas were 95:100:85 and the %RSDs (N=7) were 18.8, 21.3, and 22.1 for pHs of 2, 7, and 12, respectively. The corresponding maximum/minimum ratios were 1.59, 1.89, and 2.01. The recovery of NoDoz from the mirror was only marginally dependent on the pH and thus distilled water was used when NoDoz wipe samples were collected.

Volatility and Chromatographic Peak Shape

The chromatographic peaks for the trailing edge of the swabs obtained after dipping swabs into pH 2 water have different appearances in Figure 5b for the m/z 170 ion from 2-aminobiphenyl and Figure 7 for the m/z 121 ion from aspirin. The average peak area ratio (N=7) for the leading edge to trailing edge of the swabs was 0.39 for the m/z 171 ion and 2.07 for the m/z 121 ion. In addition, for the m/z 121 chromatogram, the trailing edge peaks were wide and the baseline often was not reached before the leading edge of the next swab reached the ionizing gas. (These differences are not explained by the different bar speeds.) The boiling point of 2-aminobiphenyl is 299°C (PTCL, 2005), while aspirin decomposes at its melting point of 138–140°C. These values suggest that volatility and/or thermal stability differences may account for the observed appearances of the peaks. As the leading edge of a swab is grazed by the nominally 300°C He

gas (Grange, 2008a), some fraction of the aspirin molecules are desorbed, ionized, and pulled into the mass spectrometer. Initially, most of the heating occurs at a small spot. The swab then blocks the gas, and a larger volume of the cotton fibers is heated. Aspirin and its decomposition products, if any, could be desorbed, transported to surfaces, and condensed on the orifice cone and elsewhere. Ions could then continue to be observed after a swab has left the ionizing gas due to desorption and ionization of aspirin and possibly its products condensed onto the cone as the gas passes between adjacent swabs giving rise to a high m/z 121 ion abundance baseline between swabs. A large portion of the aspirin exposed to the heated helium may have been desorbed, dispersed, or thermally decomposed from the trailing edge, before the swab cleared the gas and ions from the trailing edge reached orifice 1.

Description of Dispersion Experiments and Results

A small-scale, dispersive event was simulated by first pulverizing ten aspirin tablets in a mortar and pestle. The powder was inserted into the back end of an 18-in-long, 1-in inner diameter section of straight tubing affixed to a 75-in-long accordion tube that was inserted into the exhaust port of a shop vacuum. With the end of the straight tube about an inch above the driveway, the aspirin powder was blown across the driveway when the shop vacuum was run for about 2 sec. Wipe samples were acquired in a 7 x 12 grid pattern as described earlier.

A portion of the semi-quantitation ion chromatogram obtained for the aspirin wipe samples is displayed in Figure 8. A high level of carryover was evident. At this time, the literature was consulted and the low melting point and thermal lability of aspirin became apparent. Caffeine, with a sublimation point of 178°C and a melting point of 237°C (Merck &

Co., 2008), did not decompose as evidenced by the predominant $[M+H]^+$ ion in Figure 6b. Hence, it was substituted in additional simulated dispersive event experiments to avoid the possibility that the carryover was due to aspirin's thermolability. However, the observed carryover problem persisted.

Excessive Analyte

An earlier simulated dispersion experiment used 10 times as much aspirin. Aspirin or a decomposition product was clearly visible close to the discharge point, and swabs rolled across a thick layer of visible powder were caked with aspirin after wipe sample collection. The ion abundances from these swabs were saturated for the leading and trailing edges and also between the swabs. The carryover signal was saturated. Cleanup of a very visible white film on the cone and the DART and replacement of the ceramic outlet for the He source were required to remove the aspirin m/z 121 ion from mass spectra of air after this ill-advised experiment. Clearly, if a powder is visible, a relatively large amount is present and in a real-world situation such visible contamination would be included in remediation. A fifth category, "visible analyte present", was added to "high," "moderate," "low," and "non-detect" and the grid squares containing such large amounts of analyte were left unsampled. The field sampler marked the swab head with a labeling pen to alert the analyst that visible analyte was present. The corresponding squares on the semi-quantitation map were later colored in black by the analyst.

Automated cleaning of the orifice cone

A visible film of caffeine on the orifice cone was also noticed after several swabs with high

levels of analyte had been sampled by the ionizing gas even though little caffeine was visible within grid squares that were sampled. For both aspirin and caffeine, the carryover was probably due to desorption, ionization, and mass analysis of analyte that had previously condensed on the cone near the orifice. In hope of diminishing the carryover effect by cleaning the cone near the orifice, intervening swabs soaked with methanol or water were placed between wipe samples collected from the mirror onto which 375 μg of caffeine had been deposited on each square. Wipe samples collected for 10 different amounts of deposited caffeine provided 400 μg as the ion abundance saturation limit for the m/z 195 semi-quantitation ion. Both methanol and water decreased the carryover effect. Water was preferred due to its slower evaporation rate, which ensured that the first swabs wetted would remain so as the last swab was wetted immediately prior to a data acquisition. Figure 9 displays the m/z 195 ion chromatogram recorded with three adjacent wipe samples and three samples separated by air (empty holes) or swabs wetted with one, two, and three drops of water, respectively. The bottom of the trace has been magnified to better inspect the baselines between swabs. The carryover problem was most reduced when three drops of water were used, while the ion abundance from the m/z 195 ion was not noticeably depressed. After collecting data for the Al bar supporting the swabs with the highest levels of caffeine, interspersed with water-soaked swabs, a shiny region 0.5–1 cm around the orifice was observed, while film was evident farther from the orifice. We speculate that hot water vapor generated by the 300°C helium gas washed away analyte deposited near or on the edges of the orifice, partially cleaning the cone between wipe sample analyses. For the caffeine dispersion experiment, a water soaked swab was placed between all wipe samples. Even so, very large amounts of caffeine, well in excess of the 400- μg saturation level, on one or more

swabs can still cause carryover. A software solution was necessary to deal with the remaining carryover.

Lotus 123 Data Processing Macros

Text files of ion abundance vs. time were prepared by the JEOL data system for a calibration ion and for the analyte semi-quantitation ion for each data acquisition. Two data acquisitions were made for each of the three bars that supported 36, 36, and 14 wipe samples interspersed with water-soaked swabs and with calibrant swabs in the end positions. The bar speed was 0.2 cm/sec and the scan rate was 10/sec. Data were acquired for about 7 min or 2.5 min for the bar with 14 wipe samples. The text files were imported into a Lotus 123 version 9.6 (Lotus Development Corp., Cambridge, MA) spreadsheet that contained an in-house Lotus-macro-language procedure, which evolved toward greater simplicity during these experiments. The four chromatographic peak times for the calibration ion were found by examining ion abundances starting with a scan earlier than the peak time. After a scan was found with an abundance that exceeded 15% of the maximum abundance listed in the calibration ion text file, the abundances for the next 18 scans were examined to find the chromatographic peak maximum. The leading edge times for the first calibration swab in the first hole in the bar and for the second calibration swab in the last hole used (position 75, 75, or 27) and the average time width of swab heads (0.054 min) were used to predict the locations of the leading and trailing edge peaks for each wipe sample swab. Narrow time windows about the expected peak times (± 0.021 min or ± 10 scans) were examined for peaks with a threshold exceeding 500 counts. If a peak was found, the maximum for the 20-scan range was saved and compared to abundances 6 and 7 scans earlier

and later. If the maximum was less than 1.5 times any of these four abundances, a carryover plateau was being considered and the time for the expected peak and zero abundance were saved. If the peak was real, the larger of the average abundance for scans in the ranges 6-13 earlier or later were used as the average noise. The peak area was calculated as the sum of the abundance of the maximum scan and the abundances of scans recorded up to 8 scans earlier and later that exceeded the average noise (up to 17 scans). The average noise was subtracted from each abundance that was included in the sum. In this way, the larger of the two average noise values from before and after each peak was used as its baseline. The found peak and its area were saved in the list of swab times and areas. The use of narrow windows around expected times for peak maxima discriminated against artifact peaks that appeared elsewhere in the analyte ion chromatogram. As required by the mapping procedure, the completed list of times and areas contained entries for the trailing and leading edge of each swab, even if no chromatographic peak was observed. After the data for each bar was processed, the summary list was saved as a text file or appended to the previously saved list.

Figure 10 shows semi-quantitation ion chromatograms and the areas of the integrated chromatographic peaks for swabs B5-G5 from duplicate data acquisitions. The shaded areas correspond to those calculated by the Lotus procedure. The reduction in carryover for the second data acquisition was much greater than the reduction in peak areas, which was not large for the analytes investigated (Grange, 2008a). With proportionally less interference from carryover, greater weight should be assigned to the semi-quantitation map plotted from the second data acquisition.

Also notice that the carryover was much less for leading edges than for the trailing edges

in Figure 10b. Before sampling a leading or trailing edge, the hot ionizing gas bathes a region to the left or right of the orifice, respectively. Because more caffeine was desorbed for the trailing edge, more carryover was observed.

Repeat Analyses and Debris Removal

Occasionally during a data acquisition, a piece of debris on a swab was blown off and plugged the orifice, which severely decreased the observed ion abundances for later swabs. To reduce the likelihood of orifice plugging for the caffeine dispersion experiment reported here, the swabs were first run through a gas of unheated and unenergized helium with a flow of 2.6 L/min from the DART to blow off debris. The orifice was then cleaned with a methanol-soaked swab and the data was collected with the 300°C ionizing gas with the same flow. Debris removal will be more critical when flat surfaces are sampled without prior flushing with water.

Smaller Swab Tips

Figure 4b shows aspirin wipe samples acquired using swabs with 0.26-in-diameter cotton swab heads. Such large heads were subject to greater shape distortion and diameter variability during wipe sampling. Bent-over swabs altered the intra-swab distance when aligned with the support bar and could contaminate the orifice or helium gas source when rotated 90°. Figure 4c shows the smaller, 0.20-in-diameter swab heads used to collect caffeine from the driveway and interspersed swabs that were water-soaked using a pipette before analysis. These problems were reduced, and care was taken during wipe sampling to avoid bending over the cotton. The analyte was collected on a smaller amount of cotton, which should provide a larger signal, although this

hypothesis was not tested. The smaller heads were raised off the flatcars by pieces of brass rail from excess track to ensure the helium gas did not graze the top of the swabs, rather than the sides. The base of the heads of the intervening water soaked swabs were outfitted with a steel wire collar to elevate them slightly above the bar.

Dynamic Range

Figure 11 is a plot of the sum of the two chromatographic peak areas for each swab as a function of the amount of NoDoz deposited on mirror squares before triplicate wipe samples were acquired for each amount of analyte. The dynamic range was 50 over NoDoz levels between 6 and 300 μg . The plot was for the second data acquisition to minimize the effect carryover. A second experiment provided a dynamic range of 32 over levels of 12.5 to 400 μg . The average dynamic range was 41. Based on this dynamic range, a factor of 3.45 (the cube root of 41) was chosen to differentiate between high, moderate, and low levels of analyte. The high level corresponded to the maximum summed chromatographic peak area to $1/3.45$ of this level, the moderate level from $1/3.45$ to $1/(3.45)^2$ of the maximum, and the low level from $1/(3.45)^2$ to $1/(3.45)^3$ of the maximum.

Plotting the semi-quantitation map

A second Lotus 123 macro procedure plotted a semi-quantitation map after importing the text file of chromatographic peak times and areas saved by the first procedure. The user inputted only the dimensions of the sampling grid as the coordinates for the cell in the last row and last column (in this example, "G12"). The macro supports up to 25 columns and as many rows as

desired. The pairs of peak areas for each swab were summed to provide a table of cell labels, times, and areas that were used to plot the semi-quantitation map. A portion of the table is shown in Figure 12a, and maps for the first and second data acquisitions in Figures 12b and 12c, respectively.

One of four colors was copied from empty cells with these background colors based on the sums of paired areas. Red, magenta, orange, or yellow was copied into a map cell when the area from the corresponding swab was greater than $1/3.45$, $1/(3.45)^2$ to $1/3.45$, $1/(3.45)^3$ to $1/(3.45)^2$, or less than $1/(3.45)^3$ of the maximum swab area, respectively. These threshold factors of 3.45 were larger than the maximum/minimum summed area ratios observed for the sets of seven wipe samples from the mirror cells coated with a single concentration of aspirin. The cell for which a large amount of NoDoz was observed, D1, was manually colored black.

The ideal distribution of expelled NoDoz powder would be bilaterally symmetrical about the origin in the direction of the discharge and display zones of decreasing analyte levels. However, dispersion of the analyte was non-ideal. A slight breeze that blew toward the right shifted the plume in that direction. Despite vigorous and prolonged grinding with a mortar and pestle, a uniform, fine powder was not dispersed. Small clumps up to about 0.5 mm in diameter were seen. The clumps would be diverted less by the breeze and travel a shorter distance than the fine powder. The sampling grid might not have extended far enough to sample lower levels of analyte deposited only as powder. And finally, with a dynamic range of about 40, a wide range of analyte levels above the saturation level cannot be differentiated and will provide summed chromatographic peak areas from wipe sample swabs that all fall into the high level category.

In light of these observations, the semi-quantitation maps are reasonable. This simulated dispersion experiment provides evidence that a semi-quantitation map can be plotted by wipe sampling a grid pattern for compounds that are ionized by a DART ion source.

Future Work

Freshly rinsed concrete provided an ideal outdoor surface for determining the feasibility of plotting a semi-quantitation map, but does not represent real-world situations. Future experiments are planned to collect cotton-swab wipe samples from un-rinsed concrete, sand, soil, and grass. Wipe samples will be acquired through an aluminum screen resting on the surface to minimize or avoid picking up debris, sand, or soil with the swab.

Conclusion

A semi-quantitative map of chemicals dispersed by accidental, deliberate, or weather-related events can aid remediators in delineating contaminated areas, in documenting the thoroughness of the clean up with high spatial resolution, and in tracking dispersed chemicals to their source. For this work, software to plot two-dimensional semi-quantitation maps was written to complement the autosampler and field sample carrier previously built to provide rapid analyses of hundreds of samples.

Simulated dispersive events consisted of expelling powdered aspirin or NoDoz across a concrete driveway. Successful use of solvent-soaked, cotton swabs to acquire wipe samples

required selection of a solvent to pick up analytes from contaminated surfaces. Two factors were considered: the effects of a solvent on swab shape and dislocation of cotton fibers, and after water was chosen in preference to methanol and IPA, the effect of pH on the ion abundances was observed. Water with a pH of 2 provided more ion abundance for the semi-quantitation ion produced from aspirin than water with a pH of 7 or 12. The ion abundance from caffeine was independent of pH.

Wipe samples were acquired for a 7 x 12 grid pattern, by rotating the cotton swab in contact with the concrete within a 10- x 10-cm template, first from left to right and right to left, and then in the orthogonal directions of bottom to top and top to bottom. This practice evened the distribution of the analyte around the circumference of the swab.

Mass spectra were acquired from the wipe samples using the autosampler/DART/TOFMS, and newly written software was used to successfully plot a semi-quantitation map for the NoDoz distribution across the driveway. High, moderate, low, and non-detect levels of caffeine were found using ion abundance thresholds of $1/3.45$, $1/(3.45)^2$, $1/(3.45)^3$, and less than $1/(3.45)^3$ of the maximum area for the m/z 195 semi-quantitation ion observed from all swabs. Most of the 7 x 12 grid points corresponded to non-detect or high levels due to the limited size of the grid and limited dynamic range. These results justify further investigation of the feasibility of applying this technology to real-world contaminated sites: Superfund and Brownfields sites (U.S. Environmental Protection Agency, 2008a and 2008b), explosive events, and areas contaminated by weather-related events.

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Figure Captions:

Figure 1. a) the autosampler and b) the ion source with cotton swab heads inserted through an aluminum bar that is transported through the source on two N-scale model railroad flatcars.

Figure 2. The field sample carrier. Four wipe samples have been collected and the fifth cotton swab is about to be removed to acquire a wipe sample.

Figure 3. Grid pattern (7 x 12) used to collect wipe samples from the driveway.

Figure 4. a) Blank wipe samples for swabs dipped into methanol, IPA, and water; b) driveway wipe samples acquired with the larger-head swabs; and c) driveway wipe samples acquired with the smaller-head swabs. The top of swab D1 was marked to indicate that no sample was taken due to the large amount of analyte present.

Figure 5. 170.0964 ± 0.050 Da ion chromatograms for $C_{12}H_{12}N$ minus the mass of an

electron for sets of seven wipe samples for 2-aminobiphenyl on the mirror using the larger-head swabs dipped into a) isopropanol or b) water with a pH of 2. The bar speed was 0.1 cm/sec.

Figure 6. Measured masses for ions a) from aspirin with an orifice 1 voltage of 40 V and b) from NoDoz with an orifice 1 voltage of 30 V.

Figure 7. 121.02841 ± 0.050 Da ion chromatograms for sets of seven wipe samples for 125 μg of aspirin on each mirror square using swabs dipped into water with pHs of 2, 7, and 12. The bar speed was 0.2 cm/sec.

Figure 8. A portion of the semi-quantitation ion chromatogram for driveway wipe samples of aspirin.

Figure 9. Wipe samples from 375 μg of caffeine on the mirror squares not separated, separated by air, or by swabs wetted with 1, 2, or 3 drops of water. The lower portion of the trace is magnified on the y-axis to better view the baseline. Carryover is greatest for the three adjacent wipe samples and least for the three wipe samples separated by swabs soaked with three drops of water.

Figure 10. Partial semi-quantitation ion chromatograms for NoDoz wipe samples from the driveway with time and area labels. a) and b) are the first and second data acquisitions, respectively.

Figure 11. Average (N=3) of summed leading and trailing edge peak areas for wipe samples of NoDoz deposited on mirror squares.

Figure 12. a) A portion of the table containing the cell addresses and paired areas, b) the semi-quantitation map for the first data acquisition, and c) the map from the second data set. The horizontal arrow estimates the wind direction and the vertical arrow indicates the dispersal direction.