Research Article

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Semi-quantitative analysis of contaminants in soils by direct analysis in real time (DART) mass spectrometry

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RATIONALE: Cleaning up contaminated sites is a goal of the U.S. Environmental Protection Agency (EPA). A simple, high-throughput, inexpensive, selective, and specific screening method for semi-volatile, polar organic contaminants would provide high spatial resolution for monitoring remediation and for documenting successful clean ups in numerous Superfund, Brownfield, and other contaminated sites.
METHODS: An autosampler/Direct Analysis in Real Time (DART)/time-of-flight (TOF) mass spectrometer, with or without a Vapur® evacuated flange, was used to analyze 0.01–33% levels of aspirin, diphenylamine, and pentachlorophenol mixed with soil. Triplicate water-soaked swabs were manually rotated in wet analyte:soil mixtures, air dried for 2–3 h, and analyzed directly. To minimize carryover, insensitive and sensitive instrumental conditions were used to analyze high and low analyte levels, respectively. Simulated two-dimensional (2D) mapping and remediation threshold experiments were performed to test the utility of DART-TOFMS for possible sampling strategies.
RESULTS: Analyte levels differing by factors of 10 were discernible. Data were acquired for 30 swabs in 0.9 min and 3 min with helium stream temperatures of 150 °C and 250 °C and swab transport velocities of 1.45 cm/s and 0.5 cm/s, respectively. With the Vapur flange attached, the average relative standard deviations (RSDs) (n = 3) were between 16% and 40% for different analytes and analyte levels. Carryover was greatly reduced by removing the Vapur flange, but higher RSDs and occasional plugging of the cone orifice were observed.
CONCLUSIONS: A rapid, simple, rugged, and relatively inexpensive, but selective and sufficiently sensitive, semi-quantitative screening method for semi-volatile, polar, organic compounds in soil was demonstrated. The technique would provide the high spatial resolution necessary to find localized areas of high contamination within contaminated sites that might pose a risk to human and ecological health. Published 2012. This article is a US Government work and is in the public domain in the USA.

A goal of the U.S. Environmental Protection Agency (EPA) 2011–2015 Strategic Plan is "cleaning up communities and advancing sustainable development".[1] Characterizing and remediating contaminated sites within communities address this goal. Contamination from semi-volatile, polar organic compounds is present in many of the 1300 Superfund sites on the National Priorities List (NPL)[2] and 450 000 Brownfields sites estimated to exist by the EPA.[3] [A Superfund site is a site where toxic wastes have been dumped that has been designated by the EPA for remediation. Brownfield sites are sites for which reuse may be complicated by the presence of contaminants.] Of the 92 Superfund sites currently on the NPL in California,[4] 12 contain 'pesticides' and 7 contain pentachlorophenol (PCP) used for wood preservation. Dumping of chemical wastes over decades within sites could result in localized areas of very high contamination. The largest exposure risk posed by the contamination might be due to one or more of these localized areas.

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Conventional mass spectrometric methods requiring sample extraction, extract cleanup, solvent exchange, derivatization and/or chromatographic separation prior to mass analysis provide legally defensible quantitative analyses, but are expensive and time-consuming. Only a limited number of such analyses are affordable for a site, and localized areas with high contamination might be missed during initial site characterization. A rapid, simple, inexpensive, and selective screening method that can identify chemicals would provide a finer sampling grid that might find these localized areas. If necessary, conventional mass spectrometric analyses of samples from these areas could then provide the data necessary for judicial proceedings.

Direct Analysis in Real Time (DART®)/time-of-flight mass spectrometry (TOFMS) eliminates sample preparation and separation steps by analyzing samples directly. Semi-volatile, polar organic compounds are desorbed from surfaces, including soils, when inserted into a heated helium stream. The molecules are ionized by a process similar to atmospheric chemical ionization[5] and pulled into the mass spectrometer for analysis. Numerous classes of semi-volatile, polar organic compounds have been analyzed directly using DART-TOFMS,[6] including hundreds of pesticides sampled from fruit surfaces with polyurethane disks,[7] explosives on surfaces and in liquids,[8] chemical warfare agents,[9] drugs

in solvents,[10] and food packaging additives.[11] The purpose of this study was to determine the feasibility of using this technique to screen directly for compounds in contaminant: soil mixtures.

In this study, aspirin, acetaminophen, diphenylamine (DPA), and pentachlorophenol (PCP) were individually mixed into a soil to simulate contaminated soil and then sampled with cotton swabs. One or more of these analytes was tested using two simulated scenarios representative of possible site studies; mapping a two-dimensional (2D) site, and checking sample levels against a threshold. Data were acquired with and without the Vapur flange between the DART source and the TOF mass spectrometer to determine the relative advantages of the two configurations. To achieve a high throughput, the swab samples were transported through the DART-TOFMS sysyem with an in-house autosampler[12,13] to obtain analyte ion chronograms.

EXPERIMENTAL

Materials

A dry, finely screened (2 mm or less in diameter), plowed surface soil from Nebraska (USA) was used to prepare all analyte:soil mixtures. Aspirin tablets (325 mg) and acetaminophen tablets (500 mg) were purchased to serve as soil contaminants due to their low cost, bulk availability, ease of disposal as non-hazardous waste, the large amounts of analyte required, and ionization by the DART ion source. The tablets were assumed to contain the stated amounts of the drugs, which accounted for 86.3% and 87.7% of the weights of the aspirin and acetaminophen tablets, respectively, as determined from single weighings of groups of 10 tablets of each drug. A 100 g bottle of DPA (99 + % A.C.S. reagent, Aldrich, [now Sigma-Aldrich], St. Louis, MO, USA) provided an ample supply of an easily protonated analyte. A 5-g bottle of PCP (99 + %, Aldrich) provided a smaller amount of a real-world analyte. Glueless, cotton swabs with 15-cm-long wood sticks and 0.5-cm-diameter heads (REF 867-WC No Glue, Puritan Medical Products, Guilford, ME, USA) were used to collect soil samples.

Analyte/soil mixtures

The analyses were performed on swabs coated with wet analyte:soil mixtures after drying in air for at least 2 or 3 h. The swab samples were similar for both sampling schemes; not all the analytes were investigated for each scheme. All the analyte tablets or crystals were ground with a mortar and pestle to provide analyte powders. Allowance was made for the binding agents in the tablets to ensure that the mixture contained the specified percentage of analyte.

For the simulated 2D matrix experiments depicted in Fig. 1(a), analyte:soil mixtures containing from 0.1% to 33% of the analyte were prepared. The amount of soil used depended on the analyte level: 80 g, 60 g, 30 g, 15 g, 15 g, 15 g, 15 g, and 2 g for eight analyte levels of 0.01%, 0.033%, 0.1%, 0.33%, 1%, 3.3%, 10%, and 33%, respectively. Larger amounts of soil were used for the lower analyte levels to allow an accurately weighable amount of analyte to be used. For the higher analyte levels, less soil was used to limit the amount of analyte required. The analyte was added to the soil and then mixed manually within a beaker or scintillation vial (used for 15 g or less of soil) by stirring. Adding 0.16 mL of water per gram of analyte:soil mixture and stirring provided a moist mixture that provided a uniform coating on wet swabs that were inserted into and rotated within the mixtures. Slightly more water was used for the 10% and 33% analyte levels to create a paste.

For the threshold experiments represented in Fig. 1(b), 0.01–3.3% aspirin:soil batches were prepared from which portions were scooped into scintillation vials (an average of 9.7 g [n = 9]) to provide sufficient soil for the heads of the swabs to be covered. Enough water to provide soil saturation plus a small excess (3.2 mL) was added to each vial and mixed for 30 s before sampling the mud with triplicate swabs. To prepare the 10% and 33% levels, 6 g and 3 g of soil were used, respectively, and 2.4 mL of water was added to each mixture.

Sampling patterns

The simulated grid pattern used for sampling a wide range of analyte:soil mixtures is shown in Fig. 1(a) along with the positioning on three swab support bars of the cotton-swab

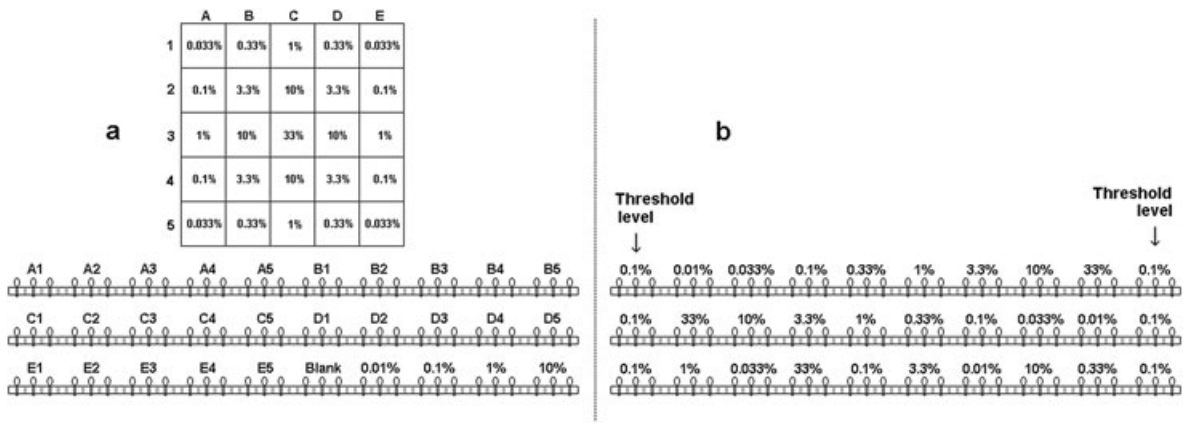

Figure 1. (a) Seven levels of analyte:soil mixtures in a simulated 2D map and (b) eight analyte:soil mixture levels compared to a 0.1% threshold standard. The vacant positions in the bars were populated with swabs to provide an easily interpreted ion chromatogram.

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samples collected for each level. The sampling pattern to determine if the aspirin:soil mixtures contained more or less analyte than a 0.1% aspirin:soil standard is shown in Fig. 1(b).

Sampling methods

For 2D mapping samples, up to 15 swabs were coated with soil from the same analyte:soil mixture. To reduce the amount of water that was added to the limited amounts of analyte:soil mixtures as swabs were rolled within the mixtures, the swabs were rolled across several layers of tissue for about 1 s to remove excess water after they had been dipped in the water for 5 s.

During the threshold experiments, for analyte levels less than 10%, the fixture shown in Fig. 2 holding three swabs was placed over the vial containing the analyte:soil mixture such that the swabs touched the bottom of the vial and the swab heads were submerged in the mud. The fixture was rotated through about 360° and back before the swabs were removed while touching the lip of the vial to remove excess mud and positioned on the support bar. For the 10% and 33% levels, single swabs were rotated in the mixture as in the grid pattern experiment.

Autosampler/DART/Vapur/TOFMS

The inexpensive autosampler designed and built in-house,[12,13] and partially shown in Fig. 3, transported swab samples through the heated helium stream from the (DART) Analysis in Real Time ion source (IonSense, Saugus, MA, USA) at a constant velocity. Recently, Chu *et al*. built and successfully used a slightly modified version of this autosampler.[16]

Figure 2. Fixture for simultaneous sampling with three cotton swabs.

The DART ion source used a heated helium (99.995%; Airgas, Inc., Radnor, PA, USA) stream containing metastable helium atoms to desorb and ionize analyte from the soil coated on the swabs. For the majority of the data acquired, the DART source was interfaced to an evacuated flange (Vapur, Ion Sense). The 4-mm, internal-diameter (i.d.) ceramic tube through the flange terminated 4 mm in front of the 400 micron i.d. inlet orifice into the mass spectrometer. The Vapur flange was affixed to a TOF mass spectrometer (AccuTOF®; JEOL, Peabody, MA, USA) which acquired all the mass spectra. The DART source and the Vapur flange are visible in Fig. 3(b).

Instrument parameters

The DART settings were not altered from those set by the manufacturer. Most of the TOFMS settings were factory-standard except for the cone temperature, which was set to 120 °C to minimize condensation and the peaks voltage which was set at 600 V to observe ions down to *m/z* 60. Several voltages were adjusted to maximize the resolving power, and detector voltages of 2100–2300 V were used. The full width at half maximum (FWHM) resolving powers were 4500, 4800, 5000, and 6600 for the *m/z* 121, 152, 172, and 266 quantitation ions, respectively. The *m/z* range acquired was 60–600 and the scan rate was set to 10/s. The optimum orifice 1 voltages were 40 V for aspirin, 35 V for acetaminophen and DPA, and 10 V for PCP. The helium flow was set to 4 L/min. The throttle valve between the evacuated flange and membrane pump was set to 10.

RESULTS AND DISCUSSION

Matrix interferences and orifice plugging

Soils are comprised primarily of minerals and organic materials. These were too involatile or non-polar to be desorbed and ionized using DART-TOFMS, as indicated by the absence of ions from these materials in the mass spectra shown in Fig. 4. The predominant ions for the 0.1% analyte:soil mixtures of aspirin, acetaminophen, and DPA were from the analytes. For the 0.1% PCP:soil, a set of isotopic, $M^{+\bullet}$ ions was formed between *m/z* 263 and 268 in much lower abundance than the most abundant precursor or product ion from the other three analytes, and low-mass, background ions predominated in the PCP spectrum shown in Fig. 4.

In earlier work[14] without the Vapur flange between the DART ion source and the TOF mass spectrometer, the orifice was occasionally plugged by debris picked up from a cement driveway when water-soaked swabs were rolled across a 100-cm^2 area. In this work, with the Vapur flange in place, plugging no longer occurred during the direct analysis of soil-coated swabs. The lack of matrix interferences and orifice plugging enabled direct analysis of analyte:soil mixtures.

Visual data interpretation

When a swab is pulled through the helium stream, analyte is desorbed, ionized, and the ions are mass analyzed as the helium stream grazes the front edge of the swab. As the swab continues through the DART helium stream, the ceramic-tube entrance into the evacuated flange (or cone orifice into the TOF mass spectrometer if the Vapur flange is not present) is

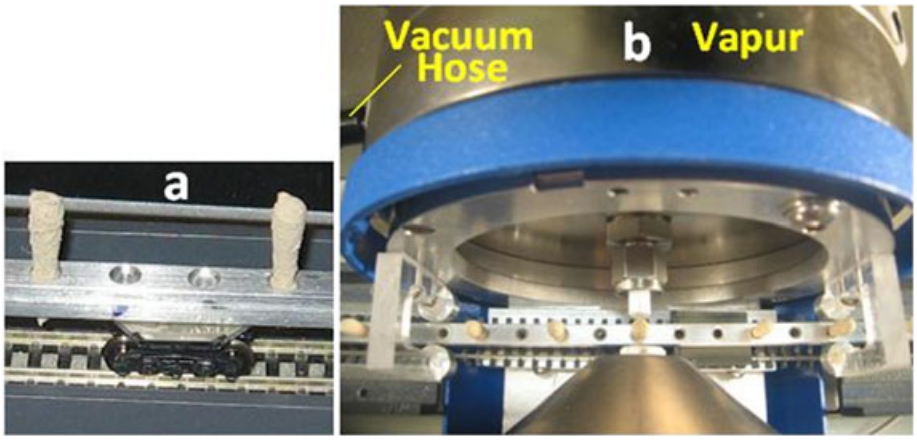

Figure 3. (a) View of one of the two wheeled supports for the bar and (b) top view of the ionization region and the swabs. The two acrylic glass and aluminum alignment devices position the swabs between the ceramic tubes of the DART ion source and the Vapur flange.

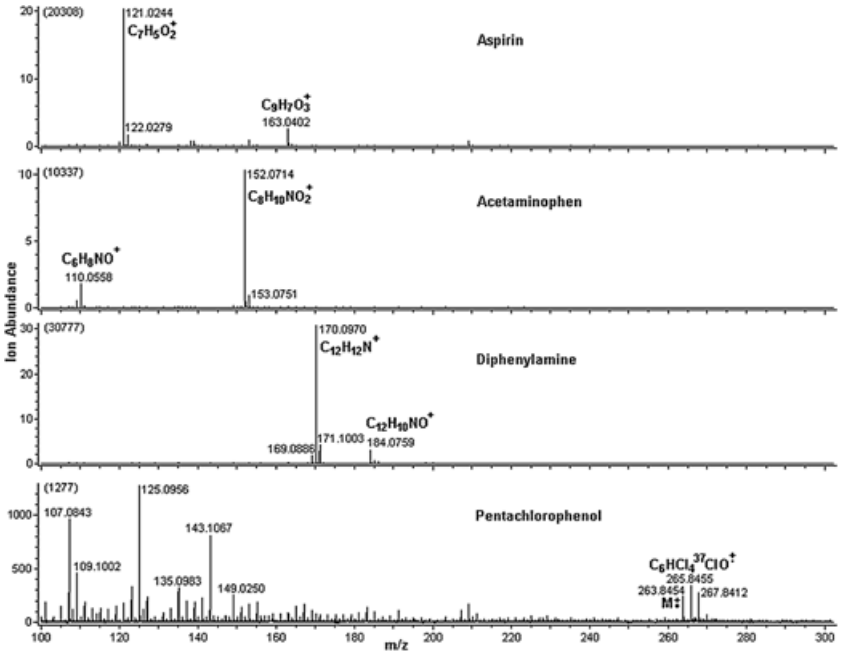

Figure 4. Mass spectra for four 0.1% analyte:soil mixtures. The semi-quantitation ions were *m/z* 121 ($C_7H_5O_2^+$), 152 ($C_8H_{10}NO_2^+$), 170 ($C_{12}H_{12}N^+$), and 266 ($C_6HCl_4{}^{37}ClO^{+\bullet}$).

blocked. Later, the helium stream grazes the trailing edge, and the ions are again mass analyzed. This sequence provided a pair of chronographic peaks for each swab, as seen in Fig. 5. If swabs occupied every position in the support bar, confusion in correlating chronographic peaks with swabs would result. By leaving a vacant position between the swabs and two vacant positions between triplicate sets of swabs, as illustrated in Fig. 1, easy to interpret ion chronograms were obtained.

Sensitivity vs. carryover

For most conventional trace analyses, the instrumental parameters are optimized to achieve a low detection limit. Such optimization would be unwise for samples with gross contamination. A contaminated site sample could have a high percentage of the contaminant, which might cause massive carryover and contamination of the mass spectrometer. To mitigate these problems, the instrumental parameters were set to limit the amount of analyte entering the instrument. The helium stream temperature was set to 150 °C to limit analyte desorption and the swabs were transported through the ionization region rapidly at 1.45 cm/s to minimize the exposure time of the swabs to the helium stream. Even so, for very high levels of aspirin and DPA with the Vapur flange present, carryover was evident. In Fig. 5, the lack of a baseline between the first and second chronographic peaks for each swab sample of 1% and 10% aspirin:soil and the broad tail after the second peak are due to carryover. For low analyte

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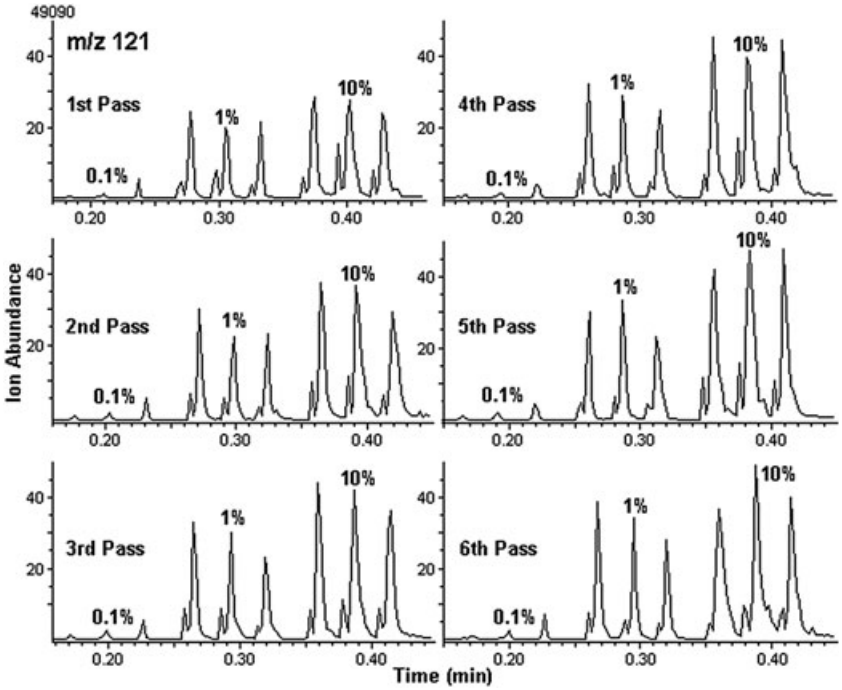

Figure 5. Normalized ion chronograms of *m/z* 121($C_7H_5O_2^+$) for multiple data acquisitions for swabs used to sample 0.1%, 1%, and 10% aspirin:soil mixtures. Conditions: 150 °C, 1.45 cm/s, and 3 h drying time.

levels, after removing swabs with high analyte levels and diluting the amount of analyte present as described later, a second analysis with a helium stream temperature set to 250 °C and a bar velocity of 0.5 cm/s was used to provide greater sensitivity.

Heat-limited ion abundances

Figure 5 shows six ion chronograms obtained with a 150 °C helium stream and a bar velocity of 1.45 cm/s for the same nine swabs coated with moist aspirin:soil mixtures after air-drying the swabs for 3 h. The sums of the paired chronographic peak areas for triplicate swab sets increased by 50%, 17%, and 26% for the 0.1%, 1%, and 10% aspirin levels, respectively, for the second pass. For the sixth pass, the corresponding increases were 50%, 32%, and 50% relative to the first pass. For all passes, the heat available from the helium stream was the same. The lowest ion abundances obtained for the first pass suggested that a portion of the heat was consumed by evaporating water still adhering to the soil after the swabs were air-dried. Acquiring similar datasets for six passes after air drying fresh swab samples from the aspirin:soil mixtures, for times of 1 to 3 h at 30 min intervals, indicated that drying times greater than 1.5 h did not further reduce this dehydration effect. To determine if oven drying would be more effective in removing water from the soil, six data acquisitions each for swab samples from 0.1% and 1% aspirin:soil and 0.1% and 1% acetaminophen:soil with a helium stream temperature of 250 °C and a bar velocity of 0.5 cm/s for sample sets air-dried for 2 h or 1.5 h followed by oven drying at 110 °C for 1 h showed similar increases in ion abundances between the first and second data acquisitions. If the heat consumption required for water removal is responsible for the lower initial abundances, the water is tightly bound. Oven drying of swabs to remove the remaining water was ineffective and would add an unnecessary step to this semi-quantitative screening procedure. For the threshold level experiment discussed later, excess water provided a mud that required a minimum air drying time of 3 h. In addition, the additional passes for the higher temperature still provided similar maximum ion abundances for the second through sixth passes. Sufficient analyte remained to ensure the ion abundance maxima were heat-limited.

The amount of heat provided by the helium stream and the exposure time of the swabs to the stream limited the maximum ion abundance observed. The maximum heights in the ion chronograms in Fig. 5 from the 1% and 10% aspirin:soil mixtures differ much less than between the 0.1% and 1% levels. For high analyte levels, the maximum ion abundance was determined primarily by the heat available rather than by the analyte concentration or by limitations of the data system or detector.

A heat-limited signal provides an advantage. Normally, only the first pass might provide data adequate to screen analyte levels in the soil. If a data acquisition problem occurred, however, Fig. 5 illustrates that a second data acquisition for the same swabs would provide acceptable data. Only data from soil samples and standards from the same pass should be compared.

Dilution of high analyte levels

Although a contaminant level of 1% or more might generally require remediation, better distinctions between levels of 1% or more were obtained by a dilution strategy that used the swabs already collected. The three swabs acquired for each analyte:soil mixture were placed into a 20-mL scintillation

vial containing 10 mL of water. The vial was capped and a vortex mixer was used to agitate the swabs within the water for 30 s, after which the swabs were removed. The water:analyte:soil slurry was remixed for 10 s to maximize the amount of suspended particulate material (including undissolved analyte) available for sampling with new swabs; the vial cap was immediately removed, and triplicate new swabs mounted into the holder shown in Fig. 2 that fit over the top of the vial were submerged to the bottom of the vial for 10 s. As the new swabs were removed with the holder, they were touched to the lip of the vial to remove excess slurry. These swabs were reinserted into the holes in the support bar from which the three original swabs had been removed and allowed to air dry for 2 h, a drying time that exceeded the 1.5 h minimum needed for moist soil coatings. After the swab samples from high contaminant levels had been replaced with the swabs dipped into the slurries, the instrumental sensitivity was increased by increasing the helium stream temperature setting to 250 °C and by reducing the support bar velocity to 0.5 cm/s. For this dilution strategy, the thickness of the soil on the swabs and the size of the swab heads should contribute more to the relative standard deviations (RSDs) than when the ion abundances are limited by the available heat. To estimate the RSDs for the dilution strategy, batches of 1%, 3.3%, and 10% aspirin:soil were prepared and five sets of triplicate swabs were sampled as described for the threshold experiments. Each set of triplicate dried swabs was placed in 10 mL of water, and the procedure just described was followed. The RSDs (n = 5) for the average paired chronographic peak areas from each set of three swabs used to sample the slurries were 35%, 22% and 17% for the 1%, 3.3%, and 10% aspirin levels, respectively.

Chronographic peak areas

Ion chronograms for the *m/z* 121 ion from aspirin on swab samples for a 2D mapping simulation are shown in Fig. 6. The initial data acquisition at 150 °C with a bar velocity of

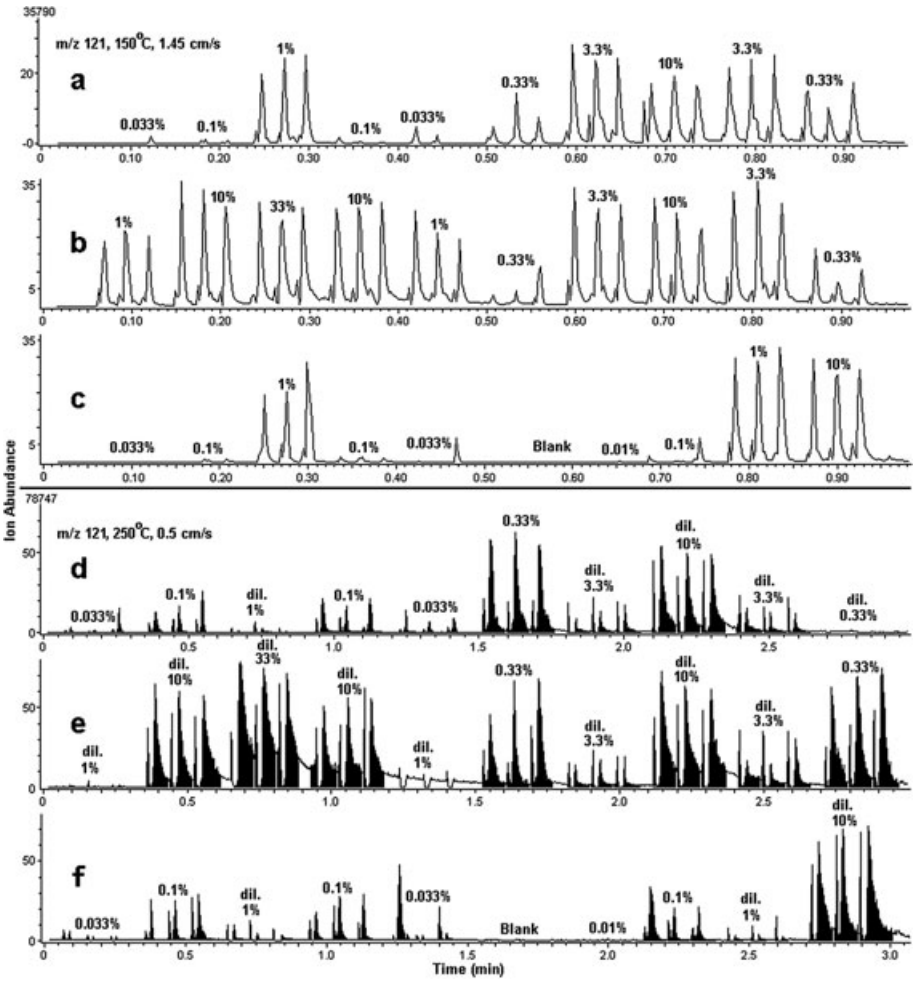

Figure 6. Ion chronograms for the *m/z* 121 ion ($C_7H_5O_2^+$) from aspirin acquired using the Vapur flange from cotton-swab samples of Blank, 0.01%, 0.033%, 0.1%, 0.33%, 1%, 3.3%, 10%, and 33% aspirin:soil mixtures in accord with the swab positions in Fig. 1(b). Traces (a), (b), and (c) were acquired with the helium steam temperature set to 150 °C and a bar velocity of 1.45 cm/s; the temperature was set to 250 °C with a bar velocity of 0.5 cm/s for traces (d), (e), and (f). Chronograms (a–c) and (d–f) were normalized to the largest peak in each triad of chronograms. The blackened areas were integrated by the Lotus macro.

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1.45 cm/s was used for screening to avoid contaminating the instrument and to determine for which swabs dilution should be used. Better-defined chronographic peaks were obtained using a bar velocity of 0.5 cm/s. To estimate the semi-quantitative capability of this technique, the average, paired ion chronographic peak areas from the triplicate swab sets obtained using a 250 °C helium stream and a 0.5 cm/s bar velocity were compared with the areas for the last four sets of swabs obtained for the 0.01%, 0.1%, 1%, and 10% aspirin:soil mixtures, which served as external standards. The areas integrated for the paired chronographic peaks for each swab are shown in black in Fig. 6. Similar ion chronograms for the DPA:soil mixtures are shown in Fig. 7. With a bar velocity of 0.5 cm/s rather than 1.45 cm/s, the orifice blockage time was sufficient for the baseline to be reestablished. The helium stream temperature increase from 150 °C to 250 °C provided more heat and more pronounced peak tails.

Carryover and peak areas

After a swab with a high level of analyte has passed through the helium stream, desorbed analyte from the swab that condensed onto the surface of the ceramic tube of the Vapur flange is desorbed, ionized, and mass analyzed to be seen as carryover in the ion chronogram. The carryover is usually insignificant while analyte is being desorbed from a swab by the available heat or the swab is blocking the entrance of the ceramic tube. The ion abundance observed when a swab is in the helium stream is due to the analyte on the swab, unless the analyte level is very small. For the diluted 1% aspirin:soil swabs (1.23–1.45 min) analyzed after the second set of diluted 10% aspirin:soil swabs, the carryover level before each pair of very small chronographic peaks was from the previously analyzed swabs. The diluted 1% aspirin:soil swabs contributed little to the carryover as is evident from the ion chronogram in Fig. 6(e) for the first set of diluted

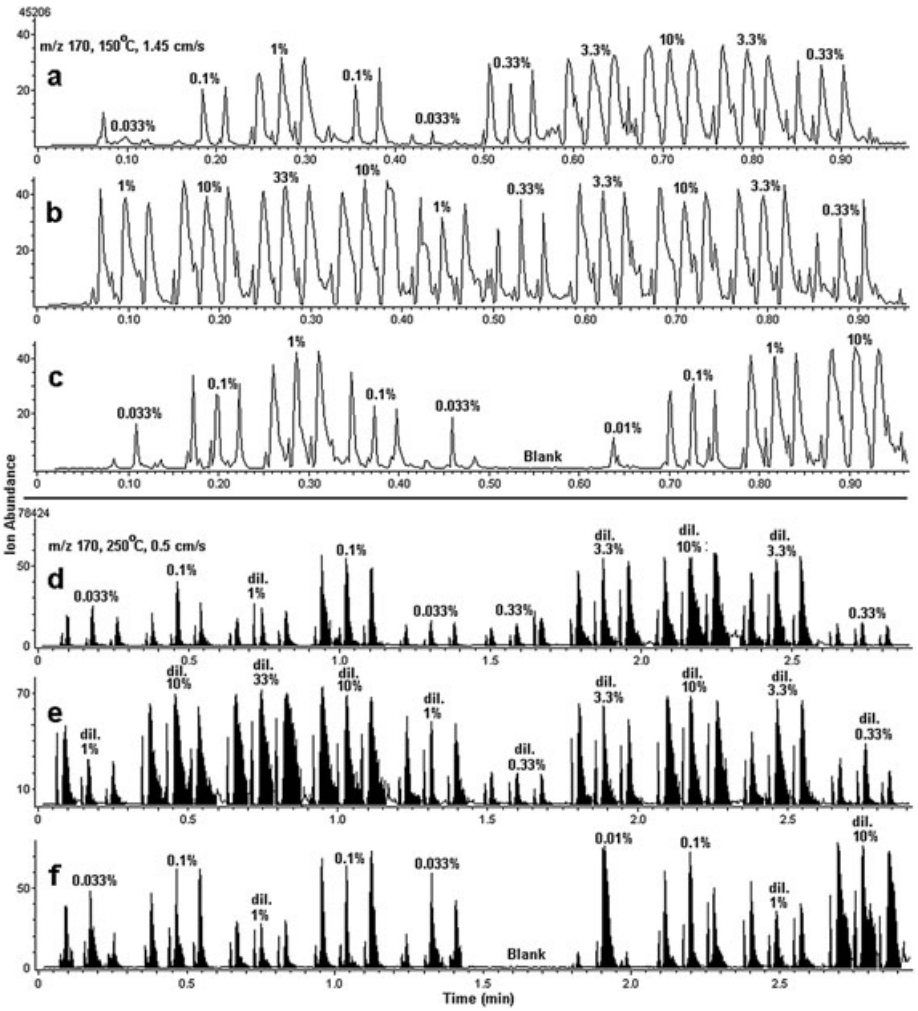

Figure 7. Ion chronograms for the *m/z* 170 ion ($C_{12}H_{12}N^+$) from DPA acquired using the Vapur flange from cotton-swab samples of Blank, 0.01%, 0.033%, 0.1%, 0.33%, 1%, 3.3%, 10%, and 33% DPA:soil mixtures in accord with the swab positions in Fig. 1(b). Traces (a), (b), and (c) were acquired with the helium steam temperature set to 150 °C and a bar velocity of 1.45 cm/s; the temperature was set to 250 °C with a bar velocity of 0.5 cm/s for traces (d), (e), and (f). Chronograms (a–c) and (d–f) were normalized to the largest peak in each triad of chronograms. The blackened areas were integrated by the Lotus macro.

1% aspirin:soil swabs traveled through the helium stream (0.05–0.3 min). For the low level of analyte on the second set of 0.1% aspirin:soil swabs, the ion abundance from the swab is superimposed onto the carryover, which must serve as the baseline for the peak integrations for this one set of triplicate swabs in the ion chronogram. For all other triplicate sets of swabs in Fig. 6(e), the original baseline before the first swab at 0.07 min was used as the baseline. Arbitrarily, if the ion abundance of each of the six chronographic peaks from a set of three swabs did not exceed twice the carryover level prior to the first peak, as was the case for the second set of diluted 1% aspirin:soil swabs, the average baseline prior to each pair of peaks was used for integration.

The hypothesis that the observed ion abundance with a swab in the helium stream is due only to the analyte on the swab and not to carryover for high levels of analyte and the integration method used is supported empirically by the observation that the RSD (n = 3) for the 33% aspirin:soil swabs shown in Fig. 6(e) improved from 50% to 17% when the original baseline for the data acquisition was used for area integration, rather than the carryover level preceding each of the three pairs of peaks. For the same two integration methods, the ratio of the average paired peak areas for the first set of 10% aspirin:soil swabs divided by the second set in Fig. 6(e) was reduced from 2.05 to 1.59 when the original baseline was used.

Residual carryover observed after running swabs with high levels of analyte can be flushed out of the system between data acquisitions by fully opening the throttle valve in the vacuum hose between the Vapur flange and the membrane pump, squirting no more than 1 mL of methanol at a time into the ceramic at the front of the evacuated flange, and observing the collapsing abundance of the predominant ion from the carryover. The throttle valve was then returned to its original setting before acquiring data for the next support bar. This process required about 5 min. The cone orifice temperature was set to 120 °C during these experiments, and contamination of the cone orifice was gradual. It was cleaned only twice over several months when the RSDs appeared to increase.

Peak area integration

High throughput requires automated integration of chronographic peak areas. Starting with a text file from the data system of the scan times and corresponding ion abundances from which the ion chronograms are plotted, a Lotus 123® macro was written to integrate the area under the chronographic peak pairs from each swab obtained with the 0.5 cm/s bar velocity. The peak pair areas were integrated for the four cases depicted in Fig. 8. In Fig. 8(a), a small amount of analyte provided very small peaks above a high baseline due to carryover for the preceding swab. In Fig. 8(b), carryover was not a significant problem. For Figs. 8(c) and 8(d), major carryover was present after a swab passed through the helium stream, and the carryover was due primarily to that swab. In Fig. 8(c), the tail area was integrated until signal was observed from the next

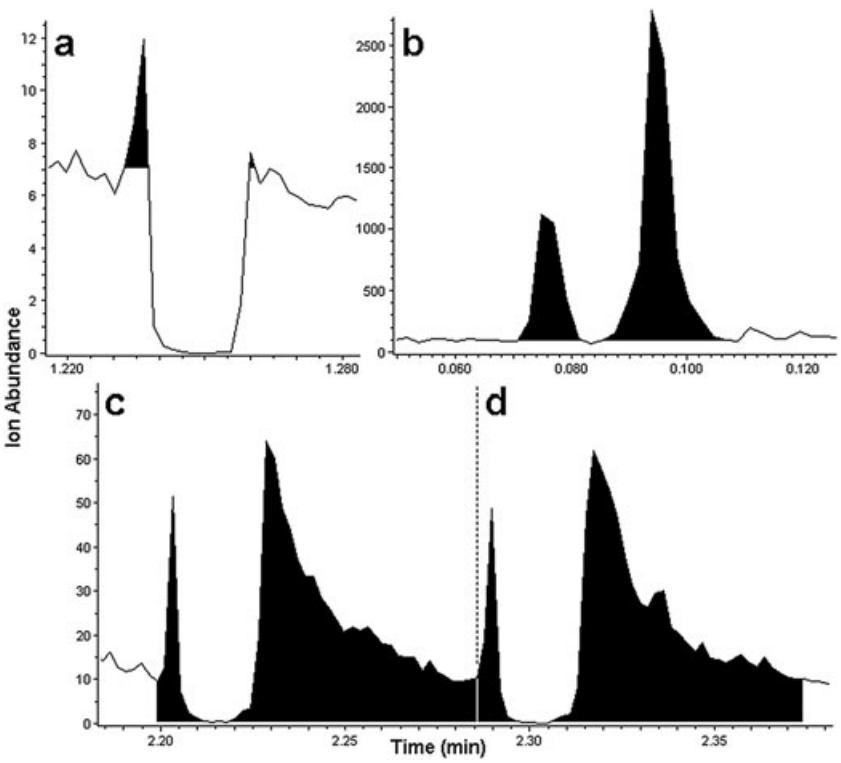

Figure 8. The paired chronographic peak areas integrated when (a) there were very small peaks above a high baseline due to carryover, (b) carryover was not a significant problem, (c) major carryover was present after a swab passed through the helium stream and another swab was located two bar positions later, and (d) two vacant positions followed the swab.

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swab, while, in Fig. 8(d), the tail area was integrated until the next swab would have provided a peak, if one were present.

In Table 1, corresponding to the ion chronograms in Fig. 6, the average (n = 3), paired chronographic peak areas are listed in ascending order. Criteria were chosen to assign analyte levels based on the four external standards analyzed last (1.85–3 min, Fig. 6(f)). If the average area was between 70% and 130% of the area for the standard, the analyte level was estimated as near that of the standard; specifically 'near 0.01%', 'near 0.1%', 'near 1%', or 'near 10%'. If the average area was between two of these ranges, the analyte level was described as 'between 0.01% and 0.1%', 'between 0.1% and 1%', or 'between 1% and 10%'. If the average was less than 70% of the 0.01% standard, the level was 'less than 0.01%', and if the average was greater than 130% of the 10% standard, the level was 'greater than 10%'. For all triplicate swab sets, the estimated analyte level was correct within a factor of 10, accuracy sufficient for a screening technique. The first of the 0.033% swabs between 1.2 and 1.5 min in Fig. 6(f) was probably contaminated with aspirin when the swabs samples were collected. The advantage of taking triplicate samples is that single outliers are obvious. In this case, the averages from the three swabs or the last two swabs both provided a correct estimate of the amount of analyte present, 'between 0.01 and 0.1%'. The average RSDs (n = 3) for the low levels of aspirin (0.01–0.33%) listed in the third column of the top half of Table 1 and the high levels of analyte (1–33%) after dilution listed in the bottom half of the table were 40% and 16%, respectively.

DPA:soil mixtures

Similar data acquired for the DPA:soil mixtures is shown in Fig. 7 and Table 2. The sensitivity was greater for DPA than for aspirin. Swabs at the 0.33% level and higher provided similar peak heights in the ion chronograms acquired using a helium stream temperature of 150 °C and a bar velocity of 1.45 cm/s and were extracted into water using the vortex mixer. As for the aspirin:soil mixtures, the estimated analyte levels were correct within a factor of 10 for all triplicate swab sets. The RSDs obtained for the low and high DPA levels in Table 2 were 24% and 19%, respectively.

Table 1. Estimated analyte levels for aspirin in aspirin:soil mixtures

Analyte level	Ave. paired peak area	%Rel. Std. Dev. (n = 3)	Estimated analyte level
0.01%	2077	31	std.[a]
0.033%	14211	66	between 0.01% and 0.1%
0.033%	22792	109	between 0.01% and 0.1%
0.033%	43743	13	between 0.01% and 0.1%
0.1%	85520	8	between 0.01% and 0.1%
0.1%	114813	13	between 0.01% and 0.1%
0.033%	118797 x[b]	109	between 0.01% and 0.1%
0.1%	137448	22	near 0.1%
0.1%	142083	49	near 0.1%
0.1%	171813	55	std.
0.33%	519019	6	between 0.1% and 1%
0.33%	523465	27	between 0.1% and 1%
0.33%	783002	13	between 0.1% and 1%
0.33%dil.[c]	1304	5[d]	between 0.1% and 1%
1%dil.	4515	24	between 0.1% and 1%
1%dil.	12140	16	between 0.1% and 1%
1%dil.	14223	54	between 0.1% and 1%
1%dil.	34842	27	std.
1%dil.	43240	15	near 1%
3.3%dil.	99806	22	between 1% and 10%
3.3%dil.	117646	12	between 1% and 10%
3.3%dil.	124044	30	between 1% and 10%
3.3%dil.	271345	7	between 1% and 10%
10%dil.	544914	5	between 1% and 10%
10%dil.	645007	7	near 10%
10%dil.	659265	13	near 10%
10%dil.	808768	14	std.
10%dil.	837824	8	near 10%
33%dil.	1197764	5	greater than 10%

[a]'std.' indicates the last data acquired for a level which was used as an external standard.
[b]'x' calls attention to the one average peak pair area that was out of order for its analyte level.
[c]'dil.' Indicates that the original swabs were extracted into 10 mL of water to dilute the amount of analyte sampled by new swabs dipped into the resulting slurry.
[d]n = 2.

Table 2. Estimated analyte levels for DPA in DPA:soil mixtures

Analyte level	Ave. paired peak area	%Rel. Std. Dev. (n = 3)	Estimated analyte level
0.01%	45883	5[a]	std.[b]
0.033%	78040	8	between 0.01% and 0.1%
0.033%	110160	18	between 0.01% and 0.1%
0.1%	152610 x[c]	47	between 0.01% and 0.1%
0.033%	248435	52	between 0.01% and 0.1%
0.033%	255417	48	between 0.01% and 0.1%
0.1%	339281	10	near 0.1%
0.1%	391265	10	near 0.1%
0.1%	409719	14	std.
0.1%	415216	32	near 0.1%
0.33%dil.[d]	92765	5	between 0.1% and 1%
0.33%dil.	120516	40	between 0.1% and 1%
1%dil.	130989	16	between 0.1% and 1%
0.33%dil.	131631	9	between 0.1% and 1%
1%dil.	196476	13	between 0.1% and 1%
0.33%dil.	204875	34	between 0.1% and 1%
1%dil.	306483	55	near 1 %
1%dil.	319563	12	std.
1%dil.	374654	18	near 1 %
3.3%dil.	454583	15	between 1% and 10%
3.3%dil.	468040	12	between 1% and 10%
3.3%dil.	480500	15	between 1% and 10%
3.3%dil.	554707	30	between 1% and 10%
10%dil.	689612	24	near 10%
10%dil.	773019	11	near 10%
10%dil.	777687	19	near 10%
10%dil.	890116	15	near 10%
10%dil.	975657	1	std.
33%dil.	1121639	19	near 10%

[a]One of the three swabs was grossly contaminated with DPA. The peak areas from only two swabs were averaged (n = 2).
[b]'std.' indicates the last data acquired for a level which was used as an external standard.
[c]'x' calls attention to the one average area that suggests an error in sample collection.
[d]'dil.' indicates that the original swabs were extracted into 10 mL of water to dilute the amount of analyte sampled by new swabs dipped into the resulting slurry.

Reducing carryover by minimizing condensation sites

The Vapur flange was removed for the following experiments to reduce carryover from the surface of the ceramic tube. Ion chronograms for the *m/z* 121 ion from aspirin are shown in Fig. 9 for a threshold determination experiment. A major reduction in carryover was observed in Fig. 9 relative to Fig. 6 with the disappearance of the broad peak tail of the second peak for swabs with high aspirin levels. The chronographic peaks became narrower, because ions produced from the edges of the swabs were collected only briefly by the 400-micron-diameter cone orifice. With the Vapur present, the 4-mm-i.d. ceramic tube directed ions toward the 400-micron-diameter cone orifice for a longer period. In past work, loose debris on a swab was occasionally carried into the cone orifice by the helium stream,[15] which plugged it, but, in dry analyte:soil pastes on the swab, soil particles adhered to each other and the swab unless they were mechanically disturbed. Plugging of the cone orifice into the TOF mass spectrometer by soil particles did not occur when, as a precaution to remove any loose soil particles, the operator blew across the swabs prior to analysis to provide a much greater flow than 4 L/min. For large numbers of analyses without the Vapur flange, assembling a device to direct a nitrogen stream across the swabs before they entered the ionization region would be advisable.

Threshold determination

To determine if remediation had reduced contaminant levels below a target value requires a single standard at that level. Triplicate swabs with 0.1% aspirin were positioned first and last on three swab support bars as the threshold standard. Triplicate swabs collected from aspirin:soil mixtures at eight aspirin levels were placed between these swabs in increasing, decreasing, and alternate low and high levels on the bars as illustrated in Fig. 1(b), and data was acquired under the two sets of conditions. For the helium stream temperature set to 150 °C and a bar velocity of 1.45 cm/s, the standard provided very small peaks (Fig. 9), while the higher levels provided large peaks. Where two or three swabs provided peaks much larger than those from the standard, a level significantly greater than that of the standard was indicated and the high-analyte-level swabs were removed before acquiring data with the temperature set to 250 °C and a bar velocity of 0.5 cm/s. For all three bars, the 1%,

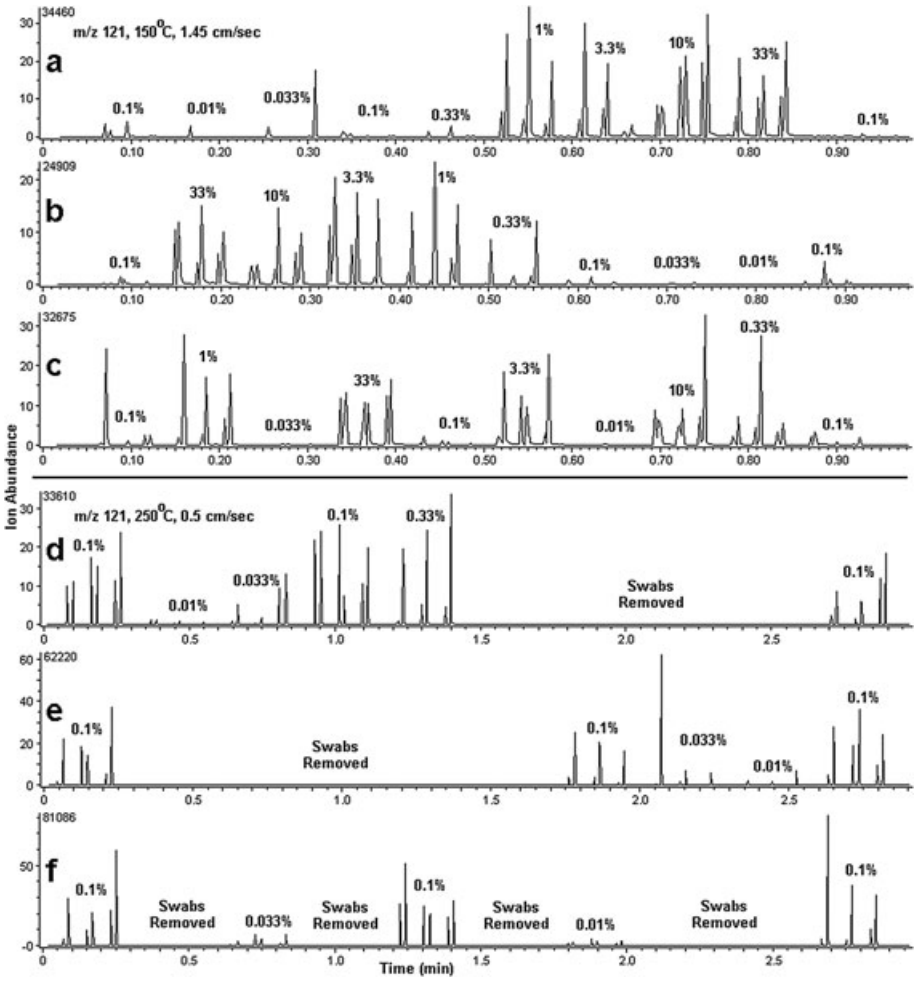

Figure 9. Ion chronograms for the *m/z* 121 ion ($C_7H_5O_2^+$) from aspirin acquired without the Vapur flange from cotton-swab samples of Blank, 0.01%, 0.033%, 0.1%, 0.33%, 1%, 3.3%, 10%, and 33% aspirin:soil mixtures. The first and last triplicate swab sets on each support bar were 0.1% aspirin used as a threshold standard. The intervening swab sets increased, decreased, and varied in aspirin level for the 1st, 2nd, and 3rd bars as depicted in Fig. 1(c). Traces (a), (b), and (c) were acquired with the helium stream temperature set to 150 °C and a bar velocity of 1.45 cm/s; the temperature was set to 250 °C with a bar velocity of 0.5 cm/s for traces (d), (e), and (f).

3.3%, 10%, and 33% levels were removed, and, for the second and third bars, the 0.33% level was also removed. Because an abnormally low maximum ion abundance was obtained for the first bar for the lower temperature, the ion chronogram displayed for the first bar in Fig. 9(a) was reacquired after data had been acquired for the other two bars and provided a maximum ion abundance similar to those of Figs. 9(b) and 9(c). To mitigate the effects of sensitivity variation over time, the threshold standard should be included on each bar.

In Table 3, the average paired peak areas are listed in increasing order. For all three bars, the 0.01% and 0.033% analyte levels were correctly found to be less than the threshold level, 0.1%. The 0.1% level sample swabs on each bar were found to be >0.1%, <0.1%, and near 0.1% using the 70–130% acceptance range. If, instead, a criterion that the average paired peak areas of a triplicate sample must be less than half of the average from the two standard swab sets was used, the <0.1% finding would be rejected. The average RSD for all entries in Table 3 was 40%.

Soil moisture content

Initial threshold detection experiments revealed a significant increase in the average paired peak areas obtained for the standard as each of nine triplicate samplings increased the water content of the remaining soil mixture. Also noteworthy was that, as shown in Tables 1 and 2, the last sampled swab sets that served as the standards provided the largest or second largest paired chronographic peak areas for each analyte level. Hence, it is important to control the moisture content of soil samples. For the data in Fig. 9 and Table 3, the amount of water present in the nine 0.1% aspirin:mud mixtures was the same, and no such systematic increase was observed for the three sets of 0.1% aspirin-level swabs for each bar.

PCP:soil mixtures

PCP used in wood preservation is a contaminant in seven California Superfund sites.[4] Four levels (0.01%, 0.1%, 1%, and 10%) of PCP:soil mixtures were prepared, and swab

Table 3. Paired peak areas and RSDs (n = 3) for the threshold experiment

Analyte level	Ave. paired peak area	%Rel. Std. Dev. (n = 3)	Estimated analyte level
0.01%	1616	52	<0.1%
0.033%	5464	62[a]	<0.1%
0.1%	35753	28	1st std.
0.1%	48058	43	>0.1% x[b]
0.1%	20472	61	2nd std.
0.33%	45178	31	>0.1%
0.01%	4449	68	<0.1%
0.033%	8300	20[c]	<0.1%
0.1%	45847	39	1st std.
0.1%	33724	36	<0.1% x[b]
0.1%	52331	21	2nd std.
0.01%	6993	30	<0.1%
0.033%	11289	39	<0.1%
0.1%	64494	55	1st std.
0.1%	69502	27	near 0.1%
0.1%	66298	43	2nd std.

[a]One swab provided 3.4 times more ion paired peak area than the other two swabs and was discarded.
[b]The finding should have been 'near 0.1%'.
[c]One swab provided almost no signal and was discarded.

samples were collected, which were air-dried, and analyzed to provide the ion chronograms shown in Fig. 10. The three lowest levels are visibly distinguishable from each other, while the dilution strategy discussed previously could differentiate between the two highest levels. The $M^{\bullet}$ radical ion was formed with the total ion abundance distributed across multiple isotopic peaks. Hence, the ion abundances were lowest for PCP. The 1% and 10% analyte level swabs were not removed before using the more sensitive conditions, because the Vapur flange was not present. In Fig. 10(b), it is shown that the carryover, although much less pronounced than if the Vapur flange were present, was still greater for the 10% analyte level than for the 1% level. The dilution strategy could be applied to provide additional evidence that the 10%-level swabs contain more PCP than the 1%-level swabs. The average RSD for the eight triplicate swab sets was 23%. The average RSD (n = 6) for the four PCP levels was 36%.

Analysis speed

The autosampler-DART-TOF mass spectrometer could be transported to a contaminated site within a van. Site characterization for semi-volatile, polar organic molecules would consist of: (1) extracting cores at grid points, (2) adding water to create mud from core samples, (3) acquiring triplicate swab samples of the mud, (4) transporting the swabs to the van, and (5) acquiring the data for rapid visual interpretation. The time required for steps (1) and (2) would depend on the size of the site and the number of grid points to be sampled. Step (3) requires less than 1 min using the fixture shown in Fig. 2. Each swab sample can be readied for analysis in the field by inserting the swab into the support bar and truncating the swab stick at the bottom of the bar with a wire cutter.[17] After at least 3 h of drying time for the last swab collected, data acquisitions require 0.9 min (1.45 cm/s) and 3 min (0.5 cm/s) for each support bar. To acquire the data depicted in Figs. 6, 7, and 9 from three bars holding a total of 90 swabs, including changing the bars between the three data acquisitions, required less than 10 min and 16 min for the 1.45 cm/s and 0.5 cm/s bar velocities, respectively. When the dilution procedure was performed, less than 3 min was required to extract each triplicate set of swabs and to acquire the swab samples of the slurry. An additional 2 h of drying time would be required before acquiring the data with a helium temperature of 250 °C and a bar velocity of 0.5 cm/s.

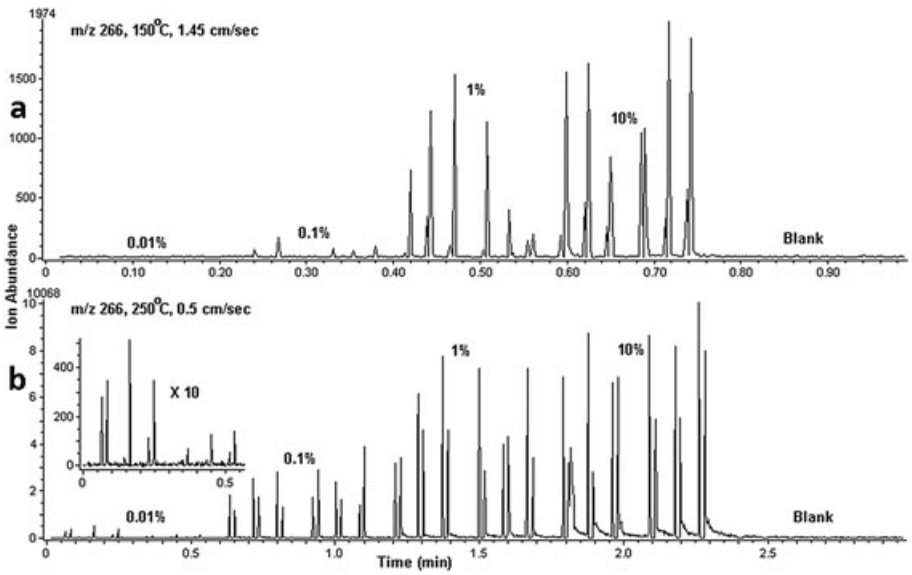

Figure 10. *m/z* 266 ($C_6HCl_4{}^{37}ClO^{\bullet}$) ion chronograms recorded without the Vapur flange with (a) a helium stream temperature setting of 150 °C and 1.45 cm/s bar velocity and (b) temperature setting of 250 °C and 0.5 cm/s bar velocity for six swab samples each of 0.01%, 0.1%, and 10% PCP:soil mixtures.

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CONCLUSIONS

A rapid, simple, and rugged, but selective and sufficiently sensitive semi-quantitative, direct screening method for semi-volatile, polar organic compounds in soil was demonstrated. The method was inexpensive relative to other mass spectral analyses that require extensive sample preparation. Analyte levels differing by factors of 10 in analyte:soil mixtures were determined over a range of 0.01–33% for aspirin, DPA, and acetaminophen (not shown) and a range of 0.01–10% for PCP. Water-soaked cotton swabs were rotated within moist or muddy analyte:soil mixtures to coat them with the mixture, allowed to air-dry, and analyzed directly using an autosampler-DART-TOF mass spectrometer. This is the first report of high-throughput, direct mass spectrometric analysis of soil mixtures.

To reduce carryover while using a Vapur flange between the DART ion source and the TOF mass spectrometer, a low helium stream temperature of 150 °C and a fast swab support bar velocity of 1.45 cm/s were used to limit analyte desorption from the soil-coated swabs. Thirty swabs were analyzed in 0.9 min. The maximum ion abundances observed were limited by the amount of heat provided by the heated helium stream for analyte desorption. For aspirin:soil and DPA:soil mixtures, similar peak heights in ion chronograms resulted for analyte levels equal to or greater than 1% and 0.33%, respectively. To achieve greater sensitivity for analyte levels less than 1% for aspirin and 0.33% for DPA, the swab samples for these and higher-level mixtures were removed from the support bars and the analysis requiring 3 min was repeated with a helium stream temperature of 250 °C and a bar velocity of 0.5 cm/s. Alternatively, the higher-level swabs were diluted mechanically into 10 mL of water using a vortex mixer. Three clean swabs were dipped into the resulting slurry, placed in the bar positions from which the original swabs were removed, allowed to dry, and re-analyzed under the more sensitive conditions. This procedure provided differentiation among the higher-levels of analyte.

The ion abundances increased with the moisture content of the soil. A small excess of water beyond the amount sufficient to create mud provided easy mixing and ensured that the soil was saturated. After a 3-h drying time, no more water evaporated from the mud-coated swabs. Most of the remaining water was evaporated from swabs during the first data acquisition. Thereafter, repeated data acquisitions provided similar ion abundances, indicating that the observed ion abundances were heat-limited. Hence, a failed data acquisition was not fatal; collecting additional swab samples at contaminated sites to acquire useful data would be unnecessary.

The Vapur flange provided lower RSDs and fewer outlying paired peak areas for triplicate analyses, and eliminated the possibility of plugging the cone orifice. Removing the Vapur flange greatly reduced carryover between swabs. Either configuration provided semi-quantitative data suitable for mapping analyte distributions within cores and across surfaces and for estimating whether an analyte level in a soil mixture was less or greater than a threshold value. Use of the Vapur flange is optional for screening analyte levels in soil.

PCP provided lower ion abundances for the $M^{+\bullet}$ radical ion than aspirin, acetaminophen, and DPA for their $[M+H]^+$ or product ions used for quantitation. Even so, PCP provided observable ion abundances at the 0.01% PCP:soil level.

Triplicate swab sample analyses occasionally revealed that one analysis was implausible compared with the other two. This multiple sample approach was practical due to the ease of sample collection and analysis speed. The average RSD (n = 3) for the data obtained for the 0.01–33% aspirin:soil mixtures was 30% and for the DPA:soil mixtures, 22% using the Vapur flange, and 40% for similar aspirin:soil data acquired without the Vapur flange.

This work demonstrated the potential for this technique to provide semi-quantitative analyte levels in soil to map contaminated areas, monitor remediation efforts, and document successful cleanups for semi-volatile, polar, organic compounds from Superfund, Brownfield, or other contaminated sites with the high spatial resolution necessary to find localized areas of high contamination that might pose a risk to human and ecological health. If preliminary analyses of sifted, contaminated soil from a site found abundant quantitation ions from the contaminants of interest, DART-TOFMS analyses could be applied to the site.

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