

Quantitation of Chemical Warfare Agents Using the Direct Analysis in Real Time (DART) Technique

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Direct analysis in real time (DART) is an ion source that permits rapid mass spectrometric detection of gases, liquids, and solids in open air under ambient conditions. It is a unique technology in the field of chemical weapons detectors in that it does not require a vapor pressure, does not require sample preparation, and is nondestructive to the original sample. While the DART technique has had success as a first line instrument of detection, there have been lingering doubts over the technique's quantitative reliability and reproducibility. Here, we demonstrate its capability to produce linear calibration curves ($R^2 = 0.99$ or better) for the nerve agents GA, GB, and VX as well as the blister agent HD. Independently prepared check standards measured against these curves typically have recovery errors less than 3%. We show the DART instrument response to be linear over roughly 3 orders of magnitude. Furthermore, this study shows that averaging as few as three measurements for each data point is sufficient to produce high quality calibration curves, thus reducing data collection time and providing quicker results.

Direct analysis in real time, termed DART, is a recent development for the ionization of volatile and nonvolatile analytes on surfaces or in solutions.^{1–4} Samples can be analyzed and identified in gaseous or condensed phases. The technique is based on the reactions of excited-state species with reagent molecules as well as polar or nonpolar analytes. In one example, excited state He interacts with atmospheric water through a series of reactions producing H_3O^+ which in many cases protonates the analyte to produce MH^+ . Other useful ionization mechanisms also occur.⁵

The DART technique has been demonstrated and documented for its effectiveness in detecting chemical warfare agents (CWAs), such as VX.^{1,3,4,6} It is a noncontact, atmospheric pressure technique that does not involve solvent wipes, extractions, or sprays; there is less toxic waste and a reduced risk of sample loss. In addition, the absence of sample preparation or chromatography allows extremely rapid analysis in time-critical situations. A faster, more accurate analysis increases the degree of safety.

DART has demonstrated success in qualitatively identifying hundreds of chemicals. Besides CWAs and their signatures (precursors, detoxification byproducts, etc.),^{1,3,4,6} pharmaceuticals,^{7–12} drugs of abuse,^{1–4,13,14} explosives,^{1,3,4,15} and biocides^{2,16,17} have been somewhat studied. Additional applications include analysis of soft drinks,¹⁸ inks,¹⁹ flavors and fragrances,²⁰ flame retardants

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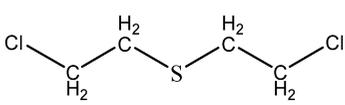
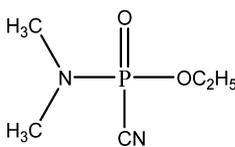
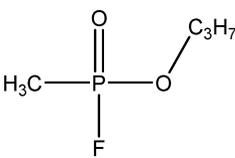
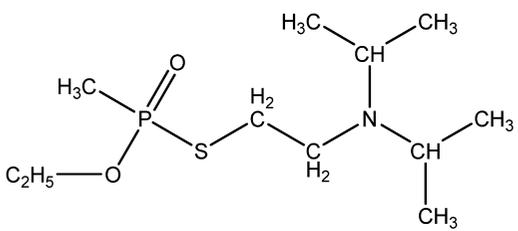
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Table 1. CWA Materials by Common Names, [CAS Number], Structure, Target Ion, and Target Ion Exact Mass

<p>Sulfur Mustard, HD [505-60-2]</p>  <p>Target Ion: $[M + OH]^+$, 174.975</p>	<p>Tabun, GA [77-81-6]</p>  <p>Target Ion: $[M + NH_4]^+$, 180.090</p>
<p>Sarin, GB [107-44-8]</p>  <p>Target Ion: $[M + NH_4]^+$, 158.075</p>	<p>VX [50782-69-9]</p>  <p>Target Ion: $[M + H]^+$, 268.150</p>

and accelerants,^{21,22} and metabolites and other biomolecules^{2,23} as well as a host of other compounds.^{24–28} However, relatively little has been published using the DART technique quantitatively.^{29,30} Therefore, we wish to report our findings on the use of DART to quantify several CWA concentrations in solution.

EXPERIMENTAL SECTION

Chemicals. *CAUTION:* Experiments with CWAs can only be conducted by specially trained personnel in a limited number of laboratories approved for handling these chemicals. The CWAs used in this study are extremely toxic and some of them are potent acetylcholinesterase (AChE) inhibitors. Extensive safety precautions were taken including the use of a 17 by 13 in. polycarbonate hood (Lab Safety Supply) around the DART source to prevent exposure to vapors. The chemical warfare agents used were Chemical Agent Standard Reference Material (CASARM) standards. They included *O*-ethyl *N,N*-dimethylphosphoramidocyanidate [77-81-6] (Tabun, GA), *O*-isopropyl methylphosphonofluoridate [107-44-8] (sarin, GB), bis(2-chloroethyl) sulfide [505-60-2] (sulfur mustard, HD), and *O*-ethyl *S*-2-diisopropylaminoethyl methyl phosphonothiolate [50782-69-9] (VX). Chemical structures, target ions, and their exact masses are given in Table 1.

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Small quantities of isotopically labeled agents, D₅-GA, D₇-GB, ¹³C₂-HD, and D₅-VX were made in house.

Ionization chemistries were chosen on the basis of two qualifications. First, the analyte should be distributed into as few ion mass channels as possible. Second, the conditions to produce these ions should be easy to create. In the case of VX (Figure 1d), the protonated neutral species is readily, and uniquely, formed under typical DART conditions. However, GA and GB have a greater tendency to form the ammonium adduct. So, when analyzing these compounds, conditions were tuned to produce only $[M + NH_4]^+$ (Figure 1b,c). Under positive ion DART conditions,¹ HD produces the $[M + OH]^+$ ion (Figure 1a). The mechanisms for the formation of these ions are still under investigation. Though the $[M + OH]^+$ ion is consistently and predictably produced by the DART chemistry, we appreciate this may not be the ideal target ion because of the potential for the misidentification of HD sulfoxide as HD. In spite of this

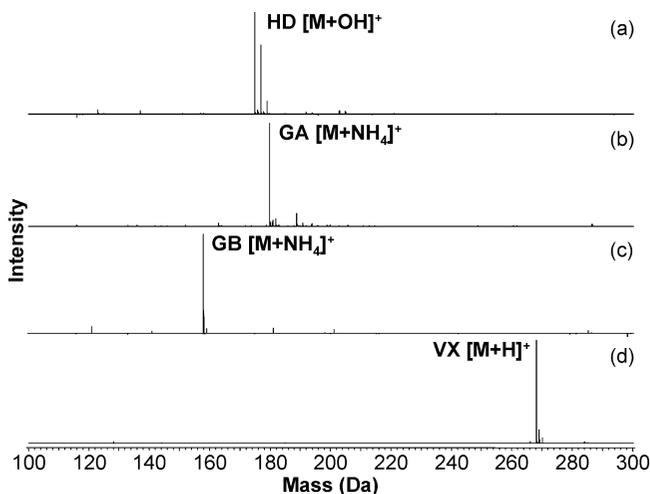


Figure 1. Mass spectra of agent standards (a) sulfur mustard (HD), (b) tabun (GA), (c) sarin (GB), and (d) VX.

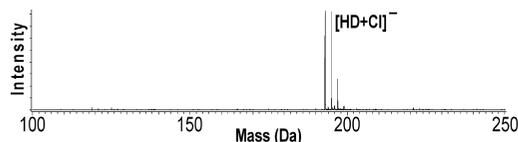


Figure 2. Negative ion mass spectrum of sulfur mustard (HD). Identification confirmed by exact mass measurement.

one potential false positive, these DART conditions have the combined benefits of minimizing mass channels, being easy to generate, and being very similar to the conditions used to generate ions of the other CWAs. This allows for rapid simultaneous detection. We feel the demonstrated advantage of real-time, multiple-agent screening outweighs a potential case of mistaken identity. However, should there be any doubt about the HD identification, HD can easily be confirmed in negative ion mode as the chlorine adduct (Figure 2).

Ion Source and Mass Spectrometer. The DART ion source has been described previously in detail.¹ In this study, the discharge electrode was set to +5000 V, while the subsequent electrodes were +150 and +250 V, respectively. DART/sample/orifice distances remained at 7 mm for this study. Gas flow rate and temperature varied. Flow typically remained around 1 L per minute while temperature ranged from 100 °C up to approximately 250 °C.

Exact mass measurements were achieved using a JEOL AccuTOF time-of-flight mass spectrometer. The mass spectrometer was operated at a resolving power greater than 6000 (fwhm definition) at mass 609. The mass scale was calibrated using neat polyethylene glycol (PEG 600) applied to a glass capillary. When necessary, a mass drift correction was made using a 0.1% solution of nicotine or a 1% solution of PEG 600. In this way, ion masses are determined to an accuracy of 2 mDa or better. Elemental compositions were confirmed by exact mass measurements.

Though broader range mass spectra are clean (Figure 1), to minimize disk space usage, mass spectra were acquired over limited ranges covering the relevant signals. These ranges were 150–190 Da for HD, 150–200 Da for GA, 135–175 Da for GB, and 260–280 Da for VX.

RESULTS

To measure an unknown quantity, an instrument response is measured against a calibration curve. One metric used to judge the quality of a calibration curve is its correlation coefficient or R^2 . This is a measure of how well the data points correlate to a linear equation. It is, therefore, indicative of the precision of the instrument because if the data points were imprecise, they would be scattered from the regression line and R^2 would not approach 1. Another test of a calibration curve is to apply it to an independently prepared sample for which the quantity is known, or check standard. Since the quantity is known, instrument accuracy is how closely its measurement matches the known quantity.

To that end, calibration standards and check standards were created. The goal was to generate calibration curves for each agent at three different quantitative levels: 1 $\mu\text{g}/\text{mL}$, 200 ng/mL , and 20 ng/mL . The last and lowest level was chosen because it

approaches safe drinking water levels.³¹ The others were selected at 10 and 50 times this lowest level. Seven calibration standards were prepared at 0%, 25%, 50%, 75%, 100%, 125%, and 150% of these quantitative levels. Another, independently prepared standard at the quantitative level is treated as the check standard. So, for example, to quantify a 200 ng/mL solution, 0, 50, 100, 150, 200, 250, and 300 ng/mL calibration standards and one 200 ng/mL check standard were prepared.

HD, GA, and GB standards were prepared in dichloromethane. These were spiked with the isotopically labeled agents, $^{13}\text{C}_2$ -HD, D_5 -GA, and D_7 -GB, respectively, as internal standard (IS). VX standards were prepared both in 2-propanol and water spiked with the isotopically labeled agent, D_5 -VX.

Solutions were sampled by dipping the closed end of a glass capillary into the solution then inserting it directly into the ion source. This process was repeated seven times for each standard. The ratio of agent signal to internal standard signal was calculated for each dip then the seven replicates averaged. It was observed that, while using the total area of agent and IS signal to calculate these ratios was best, using peak heights also produced superb results.

Calibration curves were plotted using this ratio versus concentration of agent as prepared (Figure 3). A linear least-squares regression analysis was performed using Microsoft Excel. The error associated with the measurement of agent to internal standard ratio (vertical error bars) could be quantified simply using the standard deviation of the seven replicates for each data point. Of greater concern was the error in agent concentration due to irreproducibility of pipetting volatile solvents such as dichloromethane. This error was evaluated by weighing 10 aliquots of the seven significant volumes used for dilution on an analytical balance. The resulting error (standard deviation) could then be used to calculate an error in prepared concentration (horizontal error bars). The concentration of the independent check standards were interpolated using the resulting linear equations. The resulting R^2 and percent recoveries are summarized in Table 2.

The calibration curves generated for each agent produce particularly good correlation coefficients. Plotting the residuals (Figure 3, inset), however, reveals potential but very slight nonlinearities. While the residuals do not have an abnormal number of runs, the overwhelming tendency for an individual curve to start with positive residuals, go negative, then end positive again suggests a slight higher order effect. Nevertheless, the magnitude of these effects are all but overwhelmed by the dominant linear trend.

With highly linear calibrations developed over these short ranges, the next step was to demonstrate the instrument linearity over several orders of magnitude. To do this, the three seven point GB in dichloromethane calibrations were combined to produce a 21 point calibration, spanning concentrations as little as 5 ng/mL and as much as 1500 ng/mL . This combined curve is presented in Figure 4.

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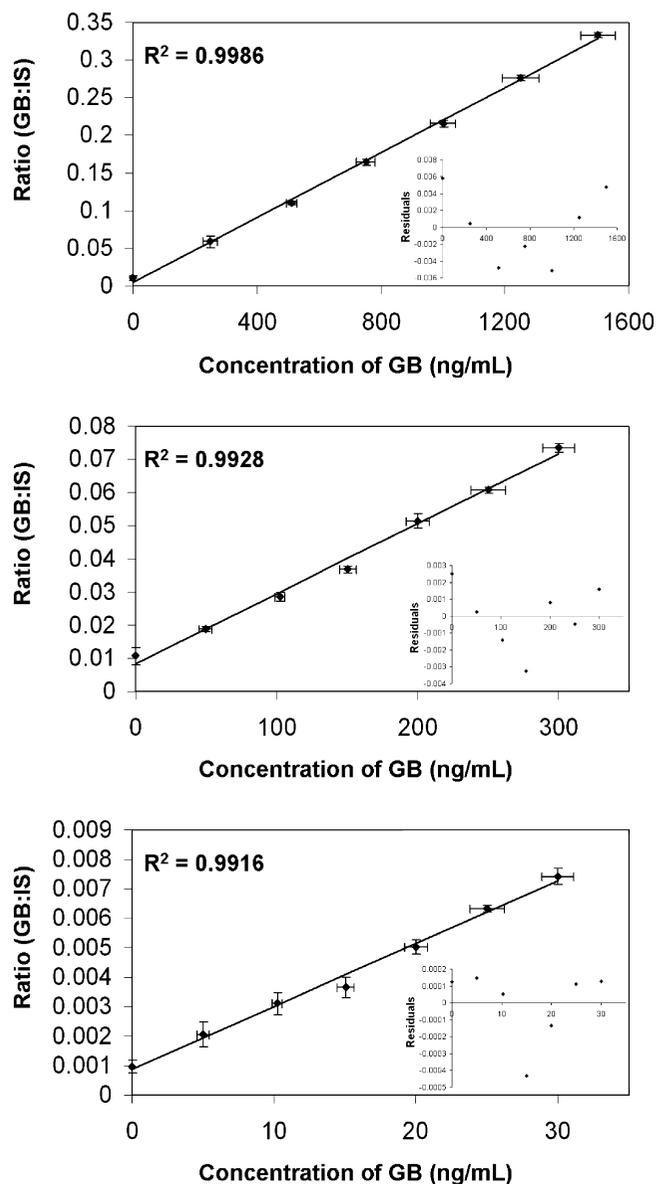


Figure 3. Calibration curves spanning 0–1500, 0–300, and 0–30 ng/mL for GB (sarin) in dichloromethane (IS is internal standard). Residuals are inset.

As stated previously, each solution was measured seven times and averaged before plotting. This number was arbitrarily chosen to be far greater than necessary to eliminate the influence of an outlying data point or gross error. As illustrated by the small error bars in the calibration curves, the scatter in the agent to internal standard ratio for each point was rather slight. In fact, the average relative error for each nonzero data point was 3.96%. This correlates well with the percent recovery data.

These results brought into question the need to average seven measurements. If five, three, or even just one measurement of each data point still produced high quality calibration curves, this would save time and, therefore, labor costs as well as reduce potential exposure time to these dangerous compounds. An investigation was performed by plotting the average for all seven measurements, then just the first five, then the first three, and finally just the first measurement. The resulting correlation

Table 2. Quantitative Results: Correlation Coefficients (R^2), Concentration of Check Standards As Prepared, Concentration Measured by DART, and Percent Recovery

range (ppb)	R^2	prepared (ppb)	measured (ppb)	recovery (%)
HD in Dichloromethane				
0–1500	0.993	1001	1035	103
0–300	0.998	200.2	197.8	99
0–30	0.9987	20.00	20.18	101
GA in Dichloromethane				
0–1500	0.993	1000	1011	101
0–300	0.998	200.1	195.2	98
0–30	0.992	19.99	20.12	101
GB in Dichloromethane				
0–1500	0.9986	1001	992.3	99
0–300	0.993	200.1	214.0	107
0–30	0.992	19.99	19.73	99
VX in 2-Propanol				
0–1500	0.997	999.2	977.7	98
0–300	0.998	199.7	195.7	98
0–30	0.994	20.00	19.64	98
VX in Water				
0–1500	0.9995	999.2	997.5	100
0–300	0.9995	199.7	195.8	98
0–30	0.9995	20.00	20.58	103

coefficients and recoveries are summarized in Table 3. Clearly, there is little advantage to averaging more than three measurements and good results are often obtained with just one.

Finally, to put the instrument to a real world test, a calibration curve was generated in muddy water from a small natural creek. The water was collected from a forested area bordered by active farm land. Possessing a brown tinge, it contained significant visible particulates as well as probable agricultural contaminants. It was used as collected, not centrifuged, or filtered in any way.

The curve (Figure 5) was generated at the lowest level for VX, 0–30 ng/mL; the scenario being, “Is this water source safe to drink?” While it is not as linear, by the measure of R^2 , as the VX plots produced in deionized water, it is still a good fit to a straight line ($R^2 = 0.992$). An independently prepared check standard of 20.01 ng/mL indicates 19.98 ng/mL, a 99.8% recovery.

This curve is a good example of when the use of signal height ratios can be superior to signal area ratios. In this particular dirty matrix, a low level background ion exists with a mass rather close to the VX ion. Close enough, in fact, that signal from this background bleeds into the VX channel. Fortunately, the physical properties of this chemical background are such that it becomes

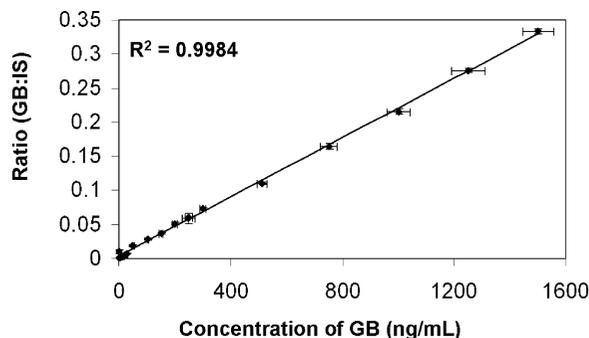
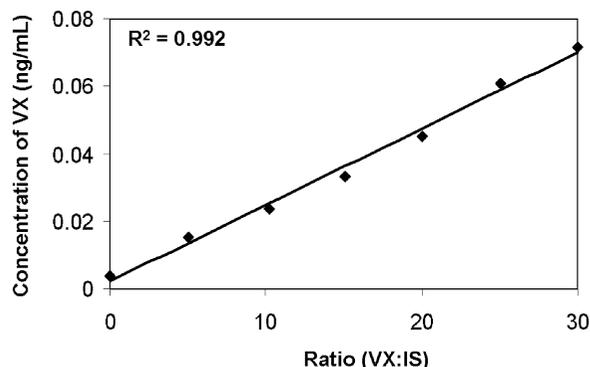
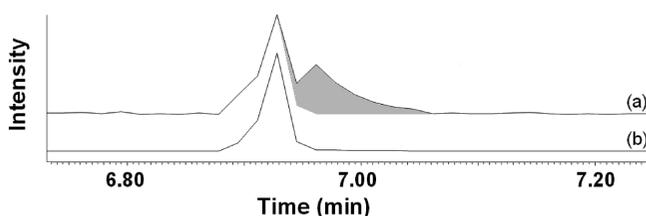


Figure 4. Combined, 21 point calibration curve for GB (sarin) in dichloromethane (IS is internal standard).

Table 3. Correlation Coefficients (R^2) Resulting from Averaging Seven, Five, Three, and One Measurement for Each of the Seven Data Points in Each Calibration Curve

	0–30 ppb	0–300 ppb	0–1500 ppb
HD in MeCl			
avg of seven	0.9987	0.9975	0.9933
avg of five	0.9986	0.9979	0.9935
avg of three	0.9970	0.9984	0.9936
single	0.9983	0.9936	0.9941
GA in MeCl			
avg of seven	0.9917	0.9975	0.9934
avg of five	0.9939	0.9972	0.9930
avg of three	0.9855	0.9969	0.9953
single	0.9803	0.9947	0.9962
GB in MeCl			
avg of seven	0.9916	0.9929	0.9986
avg of five	0.9941	0.9915	0.9986
avg of three	0.9955	0.9928	0.9986
single	0.9951	0.9862	0.9986
VX in IPA			
avg of seven	0.9936	0.9976	0.9968
avg of five	0.9925	0.9977	0.9968
avg of three	0.9991	0.9979	0.9970
single	0.9906	0.9975	0.9970
VX in DIW			
avg of seven	0.9995	0.9995	0.9996
avg of five	0.9991	0.9997	0.9994
avg of three	0.9969	0.9997	0.9996
single	0.9706	0.9993	0.9994

partially resolved over time. In thermal desorption fashion, ions from VX appear before ions from the interfering compound. So, the use of peak area would include significant signal from the interference shoulder (Figure 6). Using signal height, the effects of this background ion can be minimized. In certain cases, like

**Figure 5.** Calibration curve for VX in muddy creek water spanning 0–30 ng/mL.**Figure 6.** (a) Trace of signal with respect to time from the VX ion channel. Grey highlighted area presumed to originate from chemical background in matrix. (b) Trace of signal with respect to time from the D₅-VX (internal standard) ion channel.

this one, the thermal desorption characteristics of DART can be used as a very modest form of chromatography.

CONCLUSION

DART has proven to be an accurate, fast, nondestructive chemical agent detector in the field of identification. With this demonstration of exceptional linearity and accuracy, it should also be considered a first rate detector in the field of chemical agent quantitation comparable to tried and true chromatographic techniques such as GC/MS and LC/MS.

DART is quite quantitative with consistently outstanding correlation coefficients. The R^2 values are better than 0.99 on all 7 point and 21 point calibration curves. The linearity of the instrument has been demonstrated to be accurate across 3 orders of magnitude and current laboratory experiments suggest the linearity will hold over an even greater range.

The tried and true, widely accepted test of quantitation is the accuracy of check standards measured against calibration curves generated under the same instrument conditions. We have shown the DART technology to be capable of generating exceptional check standard recoveries. The recoveries reported in this paper were within 3% 14 out of 15 times and 7% in the worst case.

The success achieved utilizing the DART for detection and quantitative purposes does not depend on limited or constrained methodology. We have shown that accurate chemical agent identification coupled with statistically relevant quantitation can be achieved within a broad range of operational parameters. As seen, there is little to no statistical disadvantage to sampling the solution 1, 3, 5, or 7 times. This lack of hindrance allows for success given a wide range of capability both in operator and technique.

Chromatographic techniques such as GC/MS and LC/MS are very effective ways to both identify and quantify compounds such as chemical warfare agents. However, these techniques are not without complications.

During chromatography, should the elution, for a variety of reasons (temperature, time, carrier gas flow, or column overload), be incomplete, carry over can occur. To minimize carry over, a solvent blank can be run between samples. If there is no analyte in the blank, this implies there is no carry over. While running a solvent blank is good laboratory practice, it does add valuable time to an evaluation. As long as the sample does not physically contact the mass spectrometer or DART orifices, the DART-AccuTOF does not exhibit carry over.

Sample preparation for chromatographic techniques can be destructive to the original sample, such as when the analyte is adsorbed onto a surface and requires grinding and/or extraction. Time spent to ready a sample for analysis can be costly when a more rapid analysis is demanded. If extractions must be made from a solid, this material could potentially leach interfering compounds into the extraction solution. Encountering interference in the same retention time window as an analyte of interest introduces another potential obstacle in evaluation time.

Method development to achieve ideal conditions in chromatographic separations is often time-consuming and is usually completed well in advance of actual sample receipt. There is little to no quick, “on the fly”, method development available for complete unknowns.

In contrast, providing rapid analysis is where DART excels. Even a single short chromatographic run requires several minutes. By comparison, a single DART sampling requires only a few seconds. Method development typically consists of tuning the machine to maximize signal for a particular analyte and rarely requires more than a few minutes. DART's speed would be a big advantage for time critical events involving CWAs. Therefore, the biggest reason not to integrate chromatography is to maintain that speed advantage.

In the event of a chemical agent exposure, time and results are as critical as accuracy. The true advantage of utilizing the DART technology is that the results presented here are achieved not only with operator and environmental safety in mind but also with speed and accuracy as well. It is known to be an operationally safe, environmentally friendly alternative to time-consuming extractions, wipes, and sorbents. However, as we have shown, it

allows not only the opportunity to provide multiple chemical agent detection and accurate identification but also statistically excellent quantitation, all within narrow time constraints.

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