Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions

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A new ion source has been developed for rapid, noncontact analysis of materials at ambient pressure and at ground potential. The new source, termed DART (for "Direct Analysis in Real Time"), is based on the reactions of electronic or vibronic excited-state species with reagent molecules and polar or nonpolar analytes. DART has been installed on a high-resolution time-of-flight mass spectrometer (TOFMS) that provides improved selectivity and accurate elemental composition assignment through exact mass measurements. Although DART has been applied to the analysis of gases, liquids, and solids, a unique application is the direct detection of chemicals on surfaces without requiring sample preparation, such as wiping or solvent extraction. DART has demonstrated success in sampling hundreds of chemicals, including chemical agents and their signatures, pharmaceutics, metabolites, peptides and oligosaccharides, synthetic organics, organometallics, drugs of abuse, explosives, and toxic industrial chemicals. These species were detected on various surfaces, such as concrete, asphalt, human skin, currency, airline boarding passes, business cards, fruits, vegetables, spices, beverages, body fluids, horticultural leaves, cocktail glasses, and clothing. DART employs no radioactive components and is more versatile than devices using radioisotope-based ionization. Because its response is instantaneous, DART provides real-time information, a critical requirement for screening or high throughput.

Background Chronology. In early 2001, two of the authors (Laramee and Cody) began to discuss the potential applications of an atmospheric-pressure thermal electron source with capabilities similar to the Tunable Energy Electron Monochromator (TEEM).[1,2] This occurred at JEOL USA Inc. laboratories. The motivation was to extend the range of applications of the TEEM

and to develop a safe alternative to the radioactive materials, such as nickel-63 or americium-241, used in chemical agent monitors (CAM) and toxic industrial chemical sensors.

Several designs were discussed and their ion optics modeled. One of the earliest concepts made use of atmospheric-pressure electrical discharges in nitrogen and helium as a source of electrons. Following initial experiments with a prototype discharge apparatus, the gas stream from the discharge source was directed into the atmospheric pressure interface (API) of a time-of-flight mass spectrometer (AccuTOF/LC, JEOL Ltd., Akishima, Japan) in early spring of 2003. An examination of the ions produced revealed that electronic excited-state species of helium or vibronic excited-state species of nitrogen were largely responsible for sample ionization. The source was found to be highly sensitive to trace-level vapors arising from activities far removed from the laboratory, such as an open pot of glue from building renovations. Other chemicals such as acetone, acetic acid, acetonitrile, pyridine, and nitric acid could be detected from across the room by simply opening the bottle for a few hundred milliseconds (Figure S-1, Supporting Information). It was also observed that compounds could be desorbed and ionized directly from surfaces. Because of this sampling versatility, it became apparent that this device was an extremely powerful atmospheric pressure ion source that could be combined with mass spectrometry and/or ion mobility spectrometry (IMS).

The value of this new ion source as a chemical warfare agent (CWA) detector was then realized and explored. CWA testing began at the Edgewood Chemical Biological Center located at the U.S. Army Aberdeen Proving Grounds in Maryland in summer of 2003.

A decision was made to postpone publication until the initial observations could be confirmed and critical experiments could be repeated in both laboratories. DART[3] has been in continuous operation in two independent laboratories since the initial demonstration of the concept. The laboratories are located at JEOL USA, Inc. (Peabody, MA) and Edgewood Chemical Biological Center (Edgewood, MD). DART has demonstrated success in sampling hundreds of chemicals, including CWAs and their signatures (precursors, additives, reaction and degradation products, and detoxification byproducts), pharmaceutics, metabolites, amino acids, peptides, oligosaccharides, synthetic organics and organometallics, drugs of abuse, explosives, and toxic industrial

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(2) JEOL USA, Inc. Application Note MS-042503, GC/MS Analysis of Explosives by Direct Formation of Negative Ions with the TEEMmate.

(3) Patents pending.

chemicals. These were detected on various surfaces, such as porous concrete, asphalt, human skin, currency, airline boarding passes, business cards, fruits, vegetables, spices, beverages, body fluids, horticultural leaves, cocktail glasses, common laboratory equipment, and clothing.

Relationship of DART to Other Ion Sources. Electronic excited-state atoms and molecules have found use in few other ion source designs.[4−12] All of these source designs operate at reduced-pressure conditions, require sample exposure to high electrical potentials, or necessitate sample introduction into an electrical discharge, risking sample damage. Other limitations include the use of argon as the discharge working gas. However, metastable argon atoms are rapidly quenched prior to ionization in the presence of water vapor.[10] This quenching involves homolytic cleavage of the neutral water molecule without concomitant ion formation. None of the other source designs are suitable for direct analysis of solids, liquids, and gases at ambient pressure and ground potential.

The metastable atom bombardment (MAB) source of Bertrand and co-workers[4−6] relies on Penning ionization[13] at reduced pressure. Volatile samples are introduced under vacuum into a modified chemical ionization (CI) source where they are ionized by reactions with metastable atoms.

Tsuchiya and co-workers[7−9] developed a technique called Liquid Surface Penning Ionization (LPI). Ionization occurs when an atmospheric pressure beam of metastable atoms impinges on a sample-coated needle operated at kilovolt potentials. In situ sample analysis is not possible, and safety concerns require that the analysis be performed within an electrically shielded enclosure.

The Atmospheric Pressure Penning Ionization (APPeI) source developed by Hiraoka[10] makes use of a circular array of corona discharge needles in an argon atmosphere to ionize gas-phase samples. This technique is suitable only for volatile samples. Like the LPI source, the APPeI high-voltage needle array must be shielded from the operator.

Atmospheric Sampling Glow Discharge Ionization (ASGDI)[11−12] operates by introducing sample vapor through an orifice into a glow discharge region at reduced pressure. Samples must be volatile and cannot be sampled directly on surfaces. Like the APPeI source and atmospheric pressure chemical ionization (APCI) sources, the ASGDI source exposes the analyte to an electrical discharge under partial vacuum. Sample losses will occur whenever analyte is removed from a surface and introduced into a vacuum. Possible sample damage may also occur whenever

samples are exposed directly to an electrical discharge. Argon plasma cleaners are common in electron microscopy laboratories, and corona discharges have been used to destroy pollutants.[14,15]

Other atmospheric pressure ion sources in common use suffer from similar limitations. Atmospheric pressure chemical ionization (APCI)[16−19] and ElectroSpray Ionization (ESI)[20−23] require direct exposure of gaseous or vaporized liquid samples to elevated temperatures and electrical potentials. Atmospheric Pressure Photoionization (APPI)[24−27] exposes gas or vaporized liquid to short-wave ultraviolet (UV) irradiation. Atmospheric Pressure Matrix Assisted Laser Desorption (APMALDI)[28,29] requires sample dilution with a UV-absorbing matrix compound; safety concerns require an enclosed source to protect the operator from accidental exposure to laser radiation. A variant ESI technique, Desorption Electrospray Ionization (DESI),[30] has recently been reported to form ions from surfaces by exposure to electrosprayed solvent carried in a very high-velocity gas stream. Although DESI may overlap in some areas of application, DART exposes the sample to a stream of excited gas and does not require electrosprayed liquid solvent. Insufficient information exists to make further direct comparisons at this time.

EXPERIMENTAL SECTION

The DART Source. The basic DART source (Figure 1) consists of a tube divided into several chambers through which a gas such as nitrogen or helium flows. The gas is introduced into a discharge chamber containing a cathode and an anode. An electrical potential of several kilovolts initiates an electrical discharge producing ions, electrons, and excited-state species in a plasma. It is believed that the electronic or vibronic excited-state species (metastable helium atoms or nitrogen molecules) are the working reagent in DART. A detailed mechanism and supporting evidence will be presented in a follow-up paper. The gas flows into a second chamber where a second perforated electrode can be biased to remove ions from the gas stream. The

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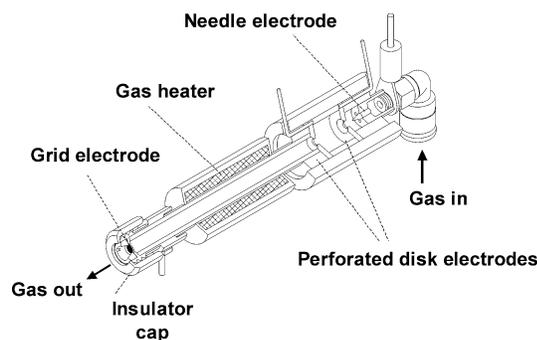(30) Takáts, Z.; Wiseman, J.; Gologan, B.; Cooks, R. G. *Science* **2004**, *306*, 471−473.

Figure 1. Cutaway view of the DART source.

Figure 2. (a) Detection of 10-ppm sodium γ-hydroxybutyrate in gin and (b) on the rim of a drinking glass. The compound is detected as the γ-hydroxybutyrate anion ($C_4H_7O_3^-$) and a characteristic $C_3H_5O_3^-$ fragment.

gas flow then passes through a third region that can be optionally heated. Gas exiting through a third perforated electrode or grid is directed toward the mass spectrometer sampling orifice; an insulating cap protects the sample and operator from any exposure to the grid. The grid serves several functions: it acts as an ion repeller and it serves to remove ions of the opposite polarity thereby preventing signal loss by ion—ion recombination. Electrons can also be produced by surface Penning ionization[31] and by oxidation of Rydberg atoms and molecules present in the gas flow. Gas flow can be directed toward a liquid or solid sample, or it can interact with vapor-phase samples.

The DART gas flow can be aimed directly toward the mass spectrometer orifice, or the gas flow can be reflected off a sample surface and into the mass spectrometer. Although optimum geometries exist for specific applications, the exact positioning, distance, and angle of DART with respect to the sample surface and the mass spectrometer are not critical.

Typical operating conditions for these experiments used a discharge needle potential of +1 to +5 kilovolts and a grounded counter electrode (first perforated disk electrode). The potentials of the second perforated electrode and the grid electrode were biased to positive potentials for positive-ion detection and to negative potentials for negative ion detection. The polarity of these electrodes was critical, but quality results were obtained with a wide range of potential values. Typical values were ±100 V and ±250 V, respectively. Gas flow rates were adjustable with typical flow rates of 1 L per minute. Gas temperature was adjustable from room temperature up to 250 °C. The DART position was adjustable on an x,y,z stage over a wide range of angles and distances. A typical DART/Sample/Orifice distance was 5 to 25 mm. However, ions could be detected even when DART was positioned 1 m away from the mass spectrometer.

Mass Spectrometer Conditions. The mass spectrometer was operated at a resolving power in excess of 6000 (fwhm definition). Orifice 1 of the atmospheric interface was set to 30 eV; ion fragmentation could be induced by increasing this potential. The mass scale was calibrated using poly(ethylene glycol) (PEG600). This produced an $[M+H]^+$ ion series in positive-ion mode (Figure S-2, Supporting Information), and a $[M+O_2-H]^-$ and $[(C_2H_4O)_n+O_2-H]^-$ ion series in negative-ion mode. Extended mass calibration was achieved by including atmospheric ions and PEG 1000. This gave a calibrated range from m/z 16 to 2000. A convenient feature of DART is that no memory effects or sample carryover
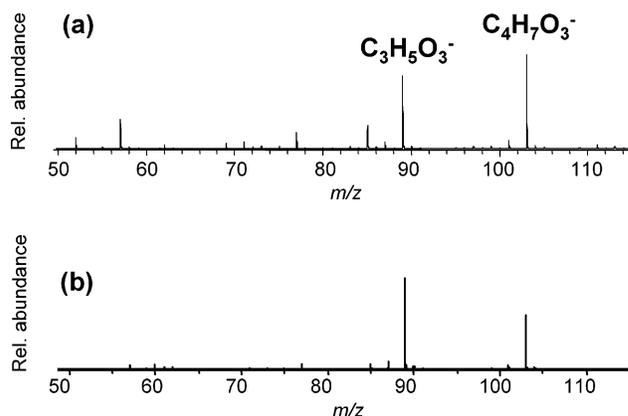
are observed. A temperature drift correction was made using calibrants of known masses. All labeled elemental compositions in this paper were confirmed by exact mass measurements.

RESULTS

Applications of DART. DART has demonstrated success in sampling hundreds of polar and nonpolar chemicals on various surfaces. Chemical classes tested include chemical warfare agents and their signatures, pharmaceutics, metabolites, peptides and oligosaccharides, synthetic organics and organometallics, drugs of abuse, explosives, and toxic industrial chemicals. These have been analyzed on concrete, asphalt, human skin, currency, airline boarding passes, business cards, fruits, vegetables, spices, beverages, body fluids, plastics, horticultural leaves, cocktail glasses, and clothing. A few representative examples are reported here.

Gamma hydroxybutyrate (GHB) is a central nervous system depressant that has been abused as a euphoric (in low doses) and as a hypnotic (at higher doses). It has received considerable attention because of its abuse as a "date-rape drug" when added to alcoholic drinks and given to unsuspecting victims. Although a rapid colorimetric assay for GHB exists,[32] the method suffers from some limitations. Most notably, ethanol produces the same colorimetric response as GHB.

DART was able to detect within seconds the presence of GHB spiked at a concentration of 10 parts-per-million into gin (Figure 2a) and 100 ng of GHB as the sodium salt deposited on the rim of a drinking glass (Figure 2b). These quantities are orders of magnitude lower than the physiological dose (typically 1 to 5 g ingested) required for the euphoric effect.

Pharmaceutical preparations in the form of tablets and capsules have been successfully revealed without breaching or opening the tablet in any way. A wide range of pharmaceutics has been examined ranging from prescription drugs, over-the-counter supplements, and veterinary medicines to confiscated illicit drugs and counterfeit preparations. The rapid detection of acetaminophen and oxycodone in a painkiller is one example (Figure 3). The active ingredients were detected within seconds without crushing, breaching, or extracting the tablet.

The detection of explosives is of great importance for forensics and security. DART has been used to detect a wide range of

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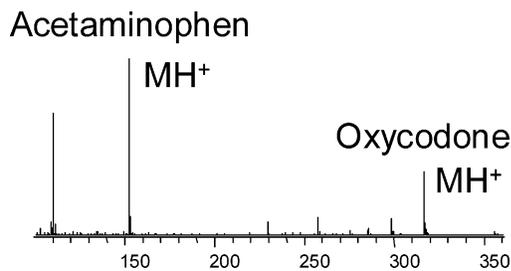
Figure 3. Rapid detection of acetaminophen and oxycodone in an intact painkiller tablet.

1. DNT
2. Amino-DNT
3. Trinitrobenzene
4. TNT
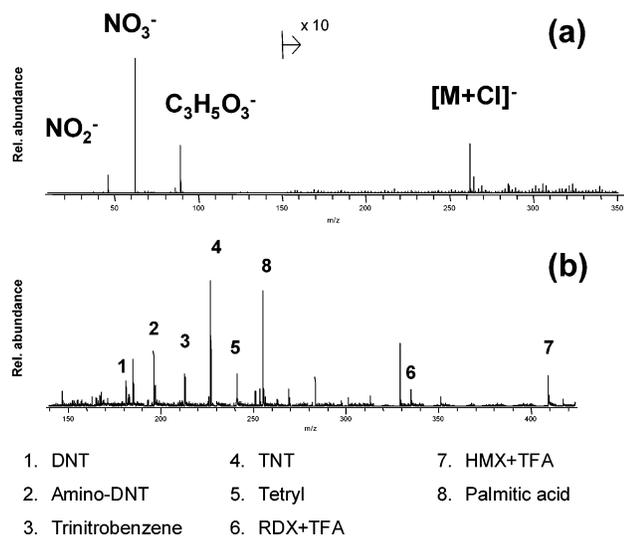5. Tetryl
6. RDX+TFA
7. HMX+TFA
8. Palmitic acid

Figure 4. (a) Nitroglycerin detected on a man's necktie 8 h after exposure to the plume from blasting at a construction site. (b) Explosives detected at a concentration of 3 ppm in water from a muddy pond. 0.1% aqueous trifluoroacetic acid was placed below the sample during the analysis to enhance formation of [M+TFA]$^-$ for RDX and HMX. The palmitic acid is a contaminant in the pond water.

explosives on various surfaces and in muddy water (Figure 4b). Organic explosives studied include nitrogen-containing substances such as dinitrotoluenes, aminodinitrotoluenes, trinitrobenzene, trinitrotoluene, nitroglycerin, ethylene glycol dinitrate, PETN, RDX, and HMX as well as the peroxide-based explosives TATP and HMTD. DART produces ions characteristic of the molecular weight for each of these compounds allowing accurate identification.

Opportunistic sampling of nitroglycerin was demonstrated using DART. Articles of clothing will absorb evidence of association with explosives. A person was walking within 1/4 mile of a construction site where dynamite was being used. Eight hours later, this person's necktie was simply placed in front of the DART ionization beam, and a small vial of dichloromethane was opened to act as a dopant. The necktie produced a peak for the chloride adduct of nitroglycerin (Figure 4a). Its identity was confirmed by exact mass measurement, which gave a mass difference of 0.00002 between the measured and theoretical m/z value of this negative ion.

Arson accelerants (Figure S-3, Supporting Information) and inorganic explosives such as ammonium nitrate, sodium azide, and sodium perchlorate (Figure S-4, Supporting Information) have also been confirmed by using DART.
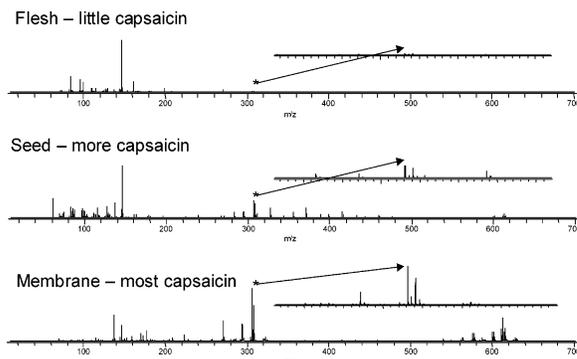

Figure 5. Distribution of capsaicin in a pepper pod. The insets show an enlarged view around the region of the capsaicin and dihydrocapsaicin [M+H]$^+$ peaks.
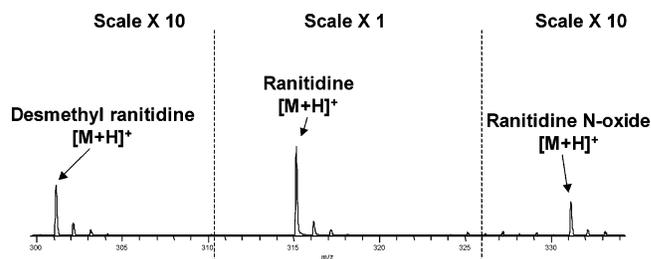

Figure 6. Urine analysis obtained in less than 30 s with DART. Ranitidine and its metabolites were detected in raw, untreated urine 5 h after ingestion of the pharmaceutical.

Foods and spices are easily analyzed by DART. The distribution of capsaicin was tracked in a red pepper pod (Figure 5). A pepper pod was sliced open with a razor blade to expose the flesh, seeds, and membrane. The different parts of the pepper were passed in front of the DART ionizing beam. Capsaicin, dihydrocapsaicin, and a related compound nonivamide were detected as the [M+H]$^+$ species with confirmed elemental compositions of $C_8H_{28}NO_3^+$, $C_8H_{30}NO_3^+$, and $C_{17}H_{28}NO_3^+$, respectively. The highest concentration was found in the membrane upon which the seeds were attached. Measurements were made within a few seconds and without any sample preparation except to cut the pepper pod open.

DART has also been applied to the analysis of bodily fluids including blood, saliva, and urine. No sample preparation was required. In all cases, a glass rod was dipped into the fluid and placed in front of the DART ionizing beam. Endogenous substances such as amino acids, urea, uric acid, creatinine, etc. as well as exogenous substances such as over-the-counter medicines, prescription drugs, and caffeine have been detected. DART can provide rapid and easy drug screening in time-critical situations.

Ranitidine is an over-the-counter medication used to prevent and treat symptoms of heartburn associated with acid indigestion and sour stomach. A person ingested a 300 mg dose, and a urine sample was analyzed with DART 5 h later. Excellent-quality mass spectra were obtained within 30 s from a glass capillary rod that was dipped into the urine (Figure 6).

The feasibility of using DART to detect chemical warfare agents has been demonstrated in preliminary studies with several members of G- and V-series nerve agents and HN-series blister agents. O-Ethyl-S-(2-iisopropylaminoethyl) methylphosphonothiolate (Agent VX) was applied to a porous concrete surface. It is readily detected after a few seconds as the protonated molecule
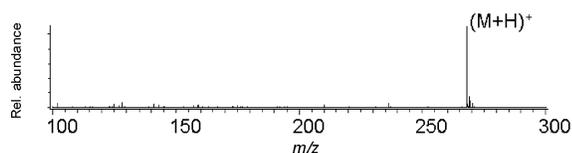
Figure 7. Detection of 788 ng American VX on a porous concrete sample.

with an excellent signal-to-background ratio of 100 000 (Figure 7). Less than 1 μg was applied. Other surfaces were also examined with the same success; these include a bird feather, asphalt, aluminum, etc. Even salts such as *N,N*-diisopropylaminoethyl methylphosphonothioic acid (EA2192) can be detected and identified with DART (Figure 8.) DART testing of other substances was equally successful. These data are available from Edgewood Chemical Biological Center (ECBC), Edgewood, MD.

DISCUSSION

Ionization Mechanism. Different ionization mechanisms occur depending upon the nature of the carrier gas, analyte concentration, and polarity of ions. A gas such as nitrogen primarily produces low-energy excited states. Thus, nitrogen will only ionize analytes that possess ionization potentials lower than the energy of the vibronic excited state. The analyte undergoes Penning ionization to form molecular ions. Fragment ions will only be produced if the corresponding neutral has sufficiently low appearance potential or sufficient large enthalpies of formation to

drive the reaction. Helium primarily produces the (2^3S) electronic excited state, which has an energy of 19.8 eV. This excited state rapidly reacts with atmospheric water (reaction 1) and has a reaction cross-section of 100 Å[2].[33] Water clusters were formed, and 14-mers were recorded (Figure 9).

$$He(2^3S) + nH_2O \rightarrow [(H_2O_{n-1})H]^+ + OH^- + He(1^1S) \quad (1)$$
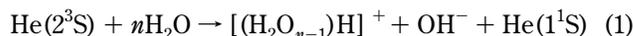
Gases capable of forming metastable species (M*) of sufficient internal energy will also produce electrons. Two general mechanisms are possible. The first mechanism produces electrons by Penning ionization of a neutral (N) (reaction 2). The second mechanism involves interaction of metastable species with a surface, such as the perforated exit electrode, to produce electrons (reaction 3).

$$M^* + N \rightarrow N^{+\bullet} + M + electron \quad (2)$$

$$M^* + surface \rightarrow M^{+\bullet} + electron \quad (3)$$
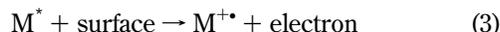
Once formed, the kinetic energies of these electrons will thermalize within a few nanoseconds. The thermalized electrons can undergo resonance electron capture with electron-loving analytes. For example, helium reacts with atmospheric water to form negative-ion clusters containing oxygen and water (Figure 10).

Corona and glow discharges carried out in the presence of even trace levels of air, such as ASGDI and corona discharge ion
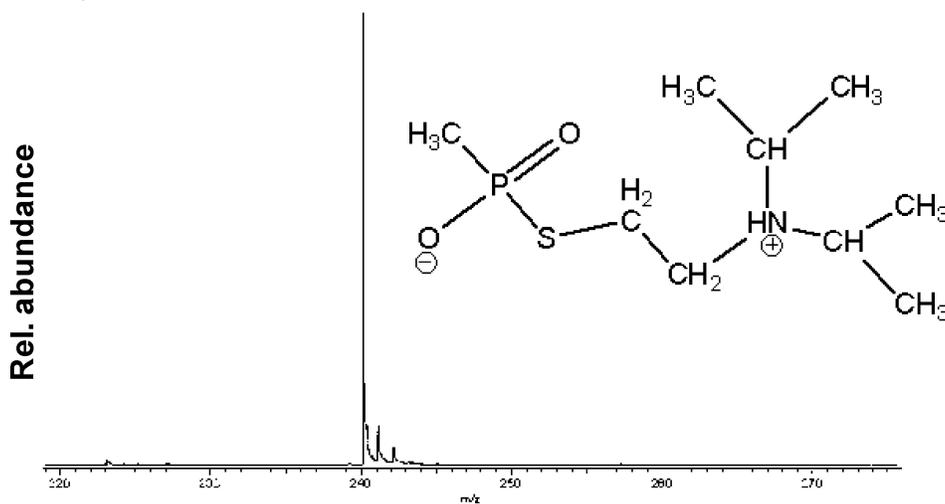

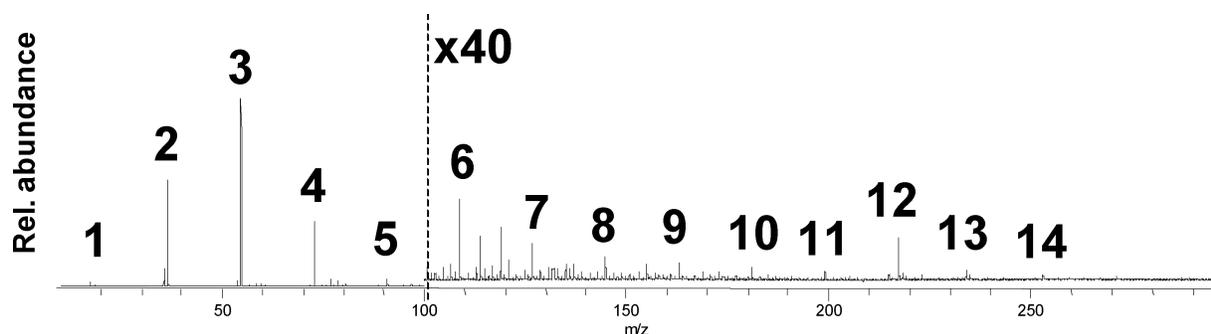**Figure 8.** EA2192, a zwitterionic derivative of American VX.

Figure 9. Ionized water clusters $[(H_2O)_nH]^+$ produced in room air by DART operated with helium carrier gas. The relatively high abundance at $n = 12$ is due to a background interference and does not indicate a "magic-number" water cluster.
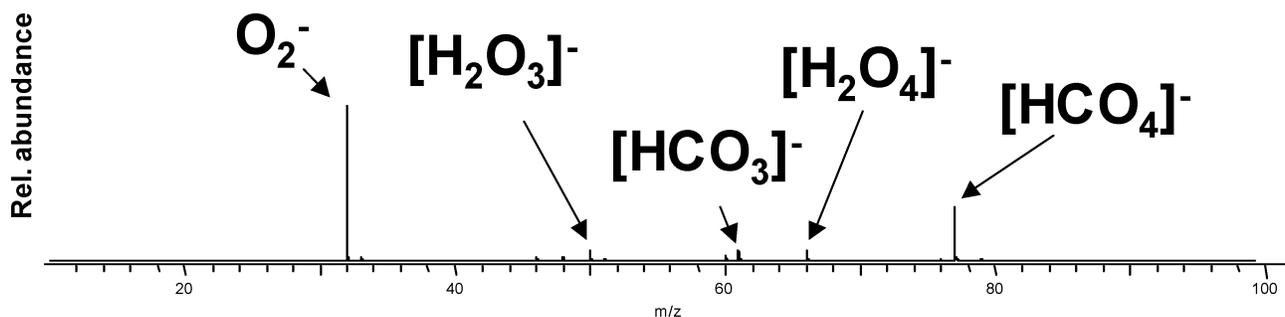
Figure 10. Negative ions produced in room air by DART operated with helium carrier gas. Note the virtual absence of nitrogen oxide ions.

mobility spectrometer sources, produce excess nitrogen oxide anions such as NO_2^- and NO_3^-, which interfere with the detection of explosives and the formation of analyte anions.[34] These nitrogen oxide anions are virtually absent in the negative-ion DART mass spectrum. Therefore, the dominant positive-ion formation mechanism is proton transfer, and the dominant negative-ion formation mechanism involves reactions of oxygen/water cluster ions.

Types of Ions Observed. Different ions are formed by DART depending on the nature of the gas, ion polarity, and whether dopants are present. Molecular ions are observed for some compounds such as toluene (Figure S-5b, Supporting Information) when nitrogen is used. Helium produces $[M+H]^+$ cations (Figure S-5a, Supporting Information). Fragment ions are not observed for all compounds; however, fragmentation can be induced by increasing the voltage on orifice 1 in the mass spectrometer atmospheric pressure interface. Adducts such as $[M+NH_4]^+$ are observed when a bottle of dilute ammonium hydroxide is opened nearby the DART source. In comparison with electrospray ionization, DART simplifies the interpretation of mass spectra of unknown compounds because alkali metal cation attachment is never observed. DART provides the additional advantage that a useful analyte signal is not weakened by spreading the ion current over more data channels than is necessary.

Negative-ion mass spectra are dominated by $[M-H]^-$ anions for most compounds. Negative charge ions $[M^{-\bullet}]$ are observed for some compounds such as nitrobenzene and TNT but not for RDX or HMX. Other adducts such as $[M+Cl]^-$ or $[M+trifluoro-acetate]^-$ are observed when a suitable dopant is present. This is advantageous for the detection of explosives such as nitroglycerine, ethylene glycol dinitrate, RDX, PETN, and HMX that do not produce molecular ions.

The surface desorption mechanism is not yet fully understood. Heating the gas aids desorption of some materials. However, salts, zwitterions, and other materials with no significant vapor pressure are easily detected by DART. For example, perchlorate anions are detected from sodium perchlorate deposited on surfaces (Figure S-4, Supporting Information).

N,N-Diisopropylaminoethyl methylphosphonothioic acid (EA2192) is a strong ionic salt that is formed upon hydrolysis of O-ethyl-S-(2-iisopropylaminoethyl) methylphosphonothiolate (Agent VX). Approximately 10% of VX is hydrolyzed into EA2192, and it is nearly as toxic as VX. It is impossible to directly analyze by GC/MS. Yet DART produces a clean mass spectrum consisting of just the MH^+ molecular cation. These materials cannot be desorbed by heat alone; therefore, other mechanisms must be involved. It is postulated that the bombardment of the surface with metastable atoms and ionized clusters aids in the desorption process.

Sensitivity. The majority of DART applications demonstrated to date have been qualitative. Although sensitivity and detection limits have not been thoroughly studied, some compounds have been detected at relatively low levels. For example, 2 pg (7 fmol) of ethyl palmitate deposited on a glass rod could be detected with a signal-to-background ratio of 70 (Figure S-6, Supporting Information). This compound is easily analyzed in a vacuum by conventional electron ionization (EI), but it is difficult to detect by atmospheric pressure ionization sources such as APCI or ESI. Although thorough quantitative studies have not been completed, it is clear that signal strength is related to sample quantity. A semiquantitative example was shown in the preceding section for the determination of capsaicin in pepper pod tissues.

CONCLUSIONS

A versatile, new ion source has been demonstrated. It is extremely useful for the rapid, noncontract analysis of substances on surfaces, liquids, and gases. No wipes or sample extractions are required. Although the full potential of the source remains to be determined, a wide variety of applications has already been explored.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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