

Direct Analysis In Real Time Mass Spectrometry (DART-MS) And Its Application

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Abstract: For Rapid mass spectral analysis of a large variety of samples the Direct analysis in real time mass spectrometry (DART-MS) this technique used. DART-MS is capable of analyzing the sample at atmospheric pressure, essentially in the open laboratory environment. It can be applied to compounds which are adsorbed or a deposited on to surfaces or that are being desorbed there from into the atmosphere. This makes DART-MS suitable and well-known for analysis of ingredients of plant materials, pesticide monitoring on vegetables, forensic and safety applications such as screening for traces of explosives, warfare agents, or illicit drugs on luggage, clothes, or bank notes, etc. DART can also be used for analysis of either solid or liquid bulk materials, as may be required in quality control, or to quickly investigate the identity of a compound from chemical synthesis. Even living organisms can be subjected to DART-MS. Driven by different needs in analytical practice, interface can be configured in multiple geometries and the combination of the DART ionization source and with various accessories to adapt the setup as required. Analysis by DART-MS relies on some sort of gas-phase ionization mechanism. By use of a corona discharge in a pure helium atmosphere which delivers excited helium atoms that, upon their release into the atmosphere. DART in which the initial generation of the ionizing the species is, and it will initiate a cascade of gas-phase reactions. In the end, this results in reagent ions created from atmospheric water or (solvent) vapour in the vicinity of the surface subject to analysis where they effect a chemical ionization process. DART ionization processes may generate negative ions or positive ions, predominantly even-electron species, but odd-electron species do also occur. Analyte properties on which the prevailing process of analyte ion formation is highly dependent.

Keywords: Direct Analysis in real time, ambient mass spectrometry, Rapid Screening Ionization.

I. INTRODUCTION

In analytical instrumentation Mass Spectrometry (MS) is one of the fastest-growing areas. The use of mass spectrometry in sup- port of synthetic, organic, and pharmaceutical chemistry is well established. Mass spectrometry is also used in materials science, environ- mental research, and forensic chemistry. It has also evolved into one of the core methods used in biotechnology. On the speed and convenience of sample analysis by mass spectrometry However, currently available ion sources place extreme restrictions. Here we report a method for using mass spectrometry to instantaneously analyze gases, liquids, and solids in open air at ground potential under ambient conditions.

In mass spectrometry Traditional ion sources used and require the introduction of samples into a high vacuum system. Traditional ion sources operated in vacuum include electron ionization (EI), chemical ionization (CI), fast atom bombardment (FAB), and field desorption/field ionization (FD/FI). These techniques have been used successfully for decades. However, the requirement that samples be introduced into a high vacuum for analysis is a severe limitation. Gas or liquid samples must be introduced through a gas chromatograph or a specially designed inlet system. By using a direct insertion probe and a vacuum lock system solid samples must be introduced. Direct insertion probes can result in vacuum failure and/or contamination of the ion source if too much sample is introduced.

Atmospheric pressure ion sources such as atmospheric pressure chemical ionization (APCI), electro spray ionization (ESI), matrix-assisted laser desorption ionization (MALDI) and atmospheric pressure photo ionization (APPI) have broadened the range of compounds that can be analyzed by mass spectrometry. However, these ion sources require that samples be exposed to elevated temperatures and electrical potentials, ultraviolet irradiation, laser radiation, or a high-velocity gas stream. Safety considerations require that the ion source be fully enclosed to protect the operator from harm.

The new ion source reported herein overcomes these limitations. The new technique, referred to as Direct Analysis in Real Time (DARTTM), has been coupled to the atmospheric pressure ionization mass spectrometer to permit high-resolution, exact mass measurements of gases, liquids, and solids. DART successfully sampled drugs of abuse, explosives, and toxic industrial chemicals, hundreds of chemicals, including chemical agents and their signatures, peptides and oligosaccharides, synthetic organics, organometallics pharmaceuticals, metabolites, pesticides and environmentally significant compounds. These chemicals were detected on a variety of surfaces such as concrete, human skin, currency, airline boarding passes, fruits and vegetables, body fluids, cocktail glasses, and clothing. The composition of drug capsules and tablets was directly analyzed.

II. BACKGROUND AND PRINCIPLE OF OPERATION

DART grew out of discussions at JEOL USA, Inc. between two of the authors (Laramée and Cody) about the possibility of developing an atmospheric pressure thermal electron source to replace the radioactive sources used in hand-held detectors for chemical weapons agents (CWAs), drugs, and explosives.



Figure 1: DSRT INSTRUMENT

DART could be used for detection of gases and liquids, led to the development of a commercial product as well as positive-ion and negative-ion non-contact detection of materials on surfaces.

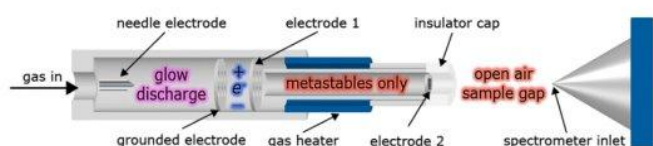
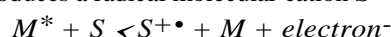


Figure 2: The DART ion source

DSRT is based on atmospheric pressure interactions of long-lived electronic excited-state atoms excited-state

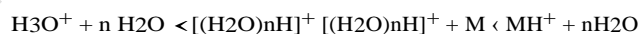
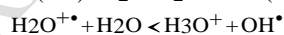
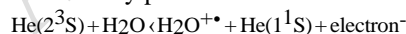
molecules with the sample and atmospheric gases. The DART ion source is shown in Figure 2. A gas (typically helium or nitrogen) flows through a chamber where an electrical discharge produces ions, electrons, and excited-state (metastable) atoms and molecules. As the gas passes through perforated lenses or grids most of the charged particles are removed and only the neutral gas molecules, including metastable species, remain. A perforated lens or grid at the exit of the DART provides several functions: it prevents ion-ion and ion-electron recombination, By surface Penning ionization, it acts as a source of electrons, and it acts as an electrode to promote ion drift toward the orifice of the mass spectrometer's atmospheric pressure interface.

Several ionization mechanisms are possible, depending on the polarity and reaction gas, the proton affinity and ionization potential of the analyte, and the presence of additives or dopants. Transfer of energy from the excited gas M^* to an analyte S having an ionization potential lower than the energy of M^* is the simplest process, involving Penning ionization. This produces a radical molecular cation $S^{+\bullet}$ and an electron (e^-).



When nitrogen or neon is used in the DART source Penning ionization is a dominant reaction mechanism. Nitrogen or neon ions are effectively removed by the electrostatic lenses and are never observed in the DART back ground mass spectrum.

The dominant positive-ion formation mechanism involves the formation of ionized water clusters when helium is used, followed by proton transfer reactions:

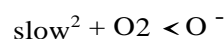


The helium 2^3S state has an energy of 19.8 eV. Its reaction with water is extremely efficient [15] with the reaction cross section estimated at 100 \AA^2 . Because of this extraordinarily- ily high cross section, DART performance is not affected by humidity.

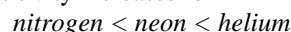
Negative-ion formation occurs by a different mechanism. Electrons (e^-) are produced by Penning ionization or by surface Penning ionization:



These electrons are rapidly thermalized by collisions with atmospheric pressure gas Thermal electrons undergo electron capture by atmospheric oxygen to produce O^- , which reacts with the analyte to produce anions.



The DART negative-ion reagent mass spectra are virtually identical for nitrogen, neon, and helium. However, negative-ion sensitivity increases for DART gases in the following order:



By Penning ionization and surface Penning ionization as the internal energy the metastable species increases and increased efficiency in forming electrons.

The polarity of the DART ion source is switched between positive-ion mode and negative-ion mode by changing the polarity of the disk electrode and grid. The plasma is not interrupted because the polarity of the discharge needle is not changed. This permits rapid switching between positive and

negative modes. Other reactions are possible. The presence of traces of do pants such as ammonium (e.g. from ammonium hydroxide headspace vapor) or chloride (e.g. from methylene chloride vapor) can modify the chemistry allowing the chemist to tailor the experiment for specific analyses.

DART produces relatively simple mass spectra characterized by M^+ ; and/or $[M+H]^+$ in positive-ion mode, and M^- or $[M-H]^-$ in negative-ion mode. Fragment ions are observed for some compounds. The degree of fragmentation can be influenced by the choice of gas, the temperature, and the AccuTOF orifice 1 potential. Alkali metal cation attachment and double-charge ions are not observed. The mechanism involved in desorption of materials from surfaces by analysis by DART of inorganic materials such as sodium perchlorate or organic salts having little or no vapor pressure is evidence of other processes. The transfer energy to the surface by metastable atoms and molecules facilitates desorption and ionization it is postulated.

In contrast with other ion sources that use metastable species, the DART ion source does not operate under reduced pressure, apply a high electrical potential to the analyte, or the analyte expose directly to the discharge plasma. Argon metastables are rapidly quenched in the presence of water vapor by a reaction involving hemolytic cleavage of the water bond without concomitant ion formation so, Argon used in many of these ion sources, is not well suited for use with DART. None of these ion sources are designed in open air under ambient conditions for direct analysis of gases, liquids, and solids.

III. APPLICATIONS

DART have a wide range of applications, such as forensic science and health, the fragrance industry, pharmaceutical industry, foods and spices.

In forensic science for analysis of explosives, drugs, inks, sexual assault evidence and of synthetic cannabinoids in herbal samples DART it can be used. A DART Forensic Database compiled from the Virginia DFS library of DART mass spectra of drugs is publicly available on the NIST website.

The deposition and release of a fragrance on surfaces such as fabric and hair is often studied in the fragrance industry. Use of DART compared to traditional methods minimizes sample amount, sample preparation, eliminates extraction steps, decreases limit of detection and analysis time.

In the pharmaceutical industry, the production and distribution of counterfeit drugs is becoming an international problem. Some countries in which this occurs are United Kingdom, China, Russia, Argentina, Nigeria and India. DART can detect active ingredients in medicine in a tablet form; there is no need for sample preparation such as crushing or extracting.

DART was used to directly analyze a red pepper pod in three different places: the placenta (white membrane onto which the seeds are attached), the seeds and the flesh of the pepper. The analyte of interest was capsaicin, a natural ingredient of a red pepper pod that is responsible for the burning sensation when eating chilies. The spectrum obtained

revealed that the highest concentration of capsaicin is in the membrane.

The DART (direct analysis in real time) ion source is a novel atmospheric pressure ionization technique, which can efficiently ionize gaseous, liquid and solid samples with high throughput. A major problem in analysis of gaseous samples is its poor detection sensitivity due to open-air sampling. Recently, a confined DART ion source (cDART) was developed, where the plasma generated by the atmospheric pressure glow discharge ionizes gas-phase molecules in a Tee-shaped flow tube instead of open air. It leads to a significant increase of the ionization efficiency of gaseous samples. In this study, the cDART source was modified and applied in online analysis of exhaled breath. The limit of detection of the improved cDART source was determined to be at the level of low ppb. The cDART source was used in the real-time monitoring of an oral anesthetic drug. The concentration variations of two active ingredients in exhaled breath, menthol and benzocaine, and their metabolites with time were obtained. The results show that the cDART ion source is a powerful analytical tool to provide high sensitivity and high throughput analysis for volatile organic compounds in human breath, and can find potential applications in clinical diagnosis and therapy.

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