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Forensic analysis of Explosive residues by direct analysis in real time mass spectrometry (DART-MS)

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Abstract

Some factors like the increasing threat, unlawful behaviour and illicit activities utilizing energetic explosive materials for felonious & criminal and terrorism activities have praised the need for a reliable, rapid techniques but also an authentic investigation technique for analyzing pivotal puzzles found at the crime scene is required. Examination of explosive residues become more tedious since the residues of origin explosive material from post-blast samples are usually trapped and fused into surrounding. Application of DART-MS. method is suitable for untreated samples or even complete objects can be examined in the open environment without affecting sample quality therefore it is useful to security investigations also. This technique has emerged as a viable method for fast, easy, and reliable "ambient ionization" for criminal investigations. In this present paper efforts have been made to highlight its significant utility to analyse different types of explosive residues due to its ability to rapidly obtain a near complete chemical profile of a sample. Review will be an informative reference document to the forensic community.

Key words: DART-MS, ambient ionization, Explosive residues analysis, direct testing of gas, liquid and solid samples and Forensic applications.

Introduction

Explosives have many legitimate uses both for civil and military purposes. In civil works they are mostly used for fireworks on festivals or any mega events ,mining of minerals, blasting of rocks, oil explorations, demolition of old derelict structures. Defence forces of all countries use explosives in large quantities in their defence or offence systems. On the other hand the abuse of explosives is extensive .These are misused by the terrorist to inflict heavy losses of life and property. They are exploited in sabotage, communal and political troubles. Moreover they are abused for murders, dacoities, revenge killing, and burglaries etc .The alarming threat of terrorism movement has engendered an urgent need of sophisticated & updated forensic explosive analysis. Forensic chemists are facing challenges like Complex matrices, limited samples, and ambiguous interpretations to establish the link between evidence to the perpetrator of the crime. The increasing threat, unlawful behaviour and illicit activities utilizing energetic explosive materials for felonious, criminal and terrorism activities have praised the need for reliable, rapid techniques but also an authentic investigation method for analyzing post blast residues found at the crime scene. Examination of explosive residues become more tedious, since the residues of origin explosive material from post-blast samples are usually trapped and fused into surrounding. To identify, to know the composition of mysterious explosive samples, needs a suitable technique to identify the both organic and inorganic ingredients of explosive materials. It is not only of great important & significant for the explosives and their post-blast residue analysis to assist forensic scientist but can also be helpful for identifying the origin of explosive material used and ultimately to help the law enforcement in narrowing down the investigation.(1)

Mass spectrometry methods play a major role in many forensic applications. While gas chromatography-mass spectrometry methods are commonly used in forensic laboratories and enforcement agencies, a variety of developed embodiment in GC-MS improved its utility and become the predominant tool to analyze the emerging issues in forensic science.Upgraded mass spectrometry methods include more versatile ionization sources, allowing the next generation of instrumentation to be more multidimensional and useful technique. DART-MS is an ambient ionization method that permits direct testing of gas, liquid and solid samples without any kind of preparation or extraction, based on thermal desorption and ionization directly from the surface of the sample under investigation.(2) and such methods are basically required for the trace evidences & post-blast samples analysis. DART stands for Direct Analysis in Real-Time. It is a version of mass spectrometry that can be applied to examine a variety of samples. With this method, untreated samples or even complete objects can be examined in the open environment without affecting sample quality thus significant for security investigations.

Direct analysis in real time (DART) has appeared as a feasible method for fast, easy, and reliable "ambient ionization" for forensic examination The ability of Direct Analysis in Real-Time to generate ions from chemicals that might be present at the scene of crime. moreover physical evidences whether they are in the gas, liquid, or solid phase can be analysed by this method with limited or small sample preparation. These advantages made this technology a useful analytical tool in numerous forensic applications (3). Thus this method has proved its utility and significance for the forensic and safety applications such as screening for traces of explosives, warfare agents, or illicit drugs on luggage, clothes, or bank notes, etc as well as for the analysis of ingredients of plant materials, pesticide monitoring on vegetables,. This technique has emerged as a viable method for fast, easy, and reliable "ambient ionization" for criminal investigations. Sisco and Forbes(4) reviewed the applications of DART-MS by providing greater context for those who may be less familiar with DART-MS, a brief discussion on the fundamentals of the technique, alternate approaches to sample analysis, and commonly employed chemo metric tools have been included by these authors. They also summarised additional resources relevant to forensic chemists with the perceived research needs and the future potential of the technique. In this present paper efforts have been made to highlight its recent development of technique specifically for the analysis of different types of explosives and their residues to provide a reference document to the forensic chemists..

Analysis of explosive residues: Review of literature

According to Nilles (5) et al the growing use of explosives by terrorists and criminals generates the need for methods and means which can rapidly analyze these energetic compounds, preferably on site. DART is an encouraging technology for surface analysis with small or no sample preparation. Authors evaluated DART ionization for use in detecting explosives on solid substrates and in liquid matrices. Fifteen explosives were selected as a consequence of their common usage. Five surfaces were selected to represent a wide range of physical properties such as porosity composition, thermal and electrical conductivity and surface morphology. Moreover these surfaces are commonly found in everyday surroundings. All the 75 compound-surface combinations generate a clear, easily noticeable, mass spectra characteristic of the aiming analyte. Simultaneous detection of five explosives was demonstrated on these same surfaces. Finally rapid detection of contamination in common fluids was also explored even present in traces.

Black demonstrated the validity of DART-MS for identification of homemade explosives using real world samples and developed a quality assured method for use in accredited forensic laboratory settings. Smokeless powder was of specific interest as there is currently no reported method to identify nitrocellulose (NC) post-blast, unless unconsumed material is recovered. Authors aimed to demonstrate the validity of DART-MS to characterize thermal breakdown products of NC and noticed that all recovered fragments were analyzed directly and in directly using full scan high resolution mass spectrometry (HRMS). Authors claimed that this study demonstrates the forensic validity of DART-MS to provide rapid and quality assured identification of explosive residues from real post-blast IED fragments (6)

Frazier et al (7) has investigated the effectiveness and limitations of different DART-MS modules for the high-throughput and sensitive detection of nineteen organic explosive residues in four different categories deposited on several substrates. The Quick strip method was applied to optimize DART gas heater temperature and dopants. Four sample introducing approaches for DART-MS involving thermal desorption transmission, , closed mesh, and direct-insert methods were applied to analyze dried and liquid samples deposited on different substrates e.g., synthetic skin, metal, plastic, fabric and leather. Authors found that representative explosives from each category could be detected with nanogram sensitivity and in less than 10 s and concluded that DART-MS can provide prompt analysis of explosives for forensic applications.

Sisco and Forbes (8) suggested the DART-MS making use of an off-axis geometry for rapid detection of nitrate ester explosives and their sugar alcohol precursors. Authors demonstrated effect of the effect of different parameters i.e., ion polarity and in-source CID on the detection of these compounds .. Sensitivity of sugar alcohols and nitrate ester explosives was observed greatest in negative ion mode with sensitivities varying from hundreds of picograms to hundreds of nanograms, which depending on the characteristics of the specific molecule. After the alteration of the in-source CID potential permitted for addition of characteristic molecular ion spectra and fragmentation spectra. In addition to above studies were carried out to identify the role of different experimental parameters on the sensitivity for these compounds. Variables so examined included the DART gas stream temperature, the presence &, the effect of a precursor on the detection of a nitrate ester explosive, accession of dopant species and the act of the analysis surface. Variable influenced the response and detection of sugar alcohols and the corresponding nitrate ester explosives. This method was said to be a useful tool in the real-world identification of homemade explosives.

Sisco et al (9) focused on one type of ambient ionization mass spectrometry, Direct Analysis in Real Time Mass Spectrometry (DART-MS or DART), and its viability as a screening tool for trace explosives analysis. They assessed the viability of the technique focusing the analysis of traces of nitro and peroxide based explosives. Parameters like optimization, reproducibility, sensitivity, development of a search library, discrimination of mixtures, and blind sampling were included in this study. Advantages and disadvantages of this technique over other similar techniques were also discussed and reported.

To identify homemade explosive residue recovered from genuine post-blast bomb fragments Black et al (10) used Direct-Analysis-in-Real-Time (DART) ionization with mass spectrometry (DART-MS).Authors designed different types of simulated improvised explosive devices to replicate post-blast debris. Peroxide-based HME was selected and used as explosive filter. Explosives namely TATP (triacetone tripe oxide,(HMTD) hexamethylene triperoxide diamine and(MEKP) methyl ethyl ketone peroxide. These IED was fired separately and the fragments so obtained were analyzed using full scan with high-resolution mass spectrometry. Fragments were examined directly and indirectly using cotton swabs and the target explosive was examined using sampling technique. The forensic validity of DART-MS was also assessed by these authors to identify the explosive residues from real post-blast IED fragments.

Gaiffe et al (11) examined 83 plastic explosives and polymer samples in less than 2 min per sample by coupling an atmospheric pressure ionization source (Direct Analysis in Real Time, DART) and a high-resolution mass spectrometer (Orbitrap) and generated the mass spectra. to avoid the difficulties in the manually interpretation and identification all of the constituent of polymers and other related significant features in the acquired mass spectra..Authors developed the systematic calculation of Kendrick mass defects (KMDs) and executed. Its use permitted the identification of the polymeric support present in each energetic formulation. by this approach the presence of polyisobutylene in PG2 was confirmed .Similarly in Semtex 10 formulation a mixture of polyisobutylene, polybutadiene, and polystyrene has been also detected & confirmed .The suggested development by these authors in the methodology allowed the notice the changes after a blast that occur in the polymeric composition of these formulations.. Results so obtained were deduced with the aid of principal component analysis and found helpful to demonstrate the main factors that differentiate the samples.

Forbes et al (12) suggested DART-MS analysis methods for the detection of inorganic explosives using high temperature thermal desorption. Authors implemented an ambient mass spectrometry platform coupled with resistive Joule heating thermal desorption and direct analysis in real time and analyzed inorganic nitrate, nitrite, chlorate & per chlorate salts. The resistive heating component produced discrete and rapid heating ramps and elevated temperatures, by passing a few amperes of DC current through a nichrome wire temperature raised more or less up to 400 °C s−1 and 750 °C,. Joule heating thermal desorption increased the applicability and capability of traditionally used DART-MS for the trace analysis of inorganic compounds that was previously much more difficult for the analysis To get the systematic evaluation of five system parameters authors implemented a partial factorial design of experiments .A base set of conditions for coupling of Joule heating thermal desorption with DART-MS was also derived with this evaluation and authors demonstrated sensitive detection of a range of inorganic oxidizer salts, lower to single nanogram levels. Design of experiments also characterised Joule heating thermal desorption filament current and in-source collision induced dissociation energy as inducing the greatest effect on system response. Tuning of Joule heating thermal desorption current provided a method for controlling the correlative degrees of thermal desorption and thermal decomposition. Furthermore, in-source collision induced dissociation provided manipulation of adduct and cluster fragmentation, optimizing the detection of molecular anion species. Authors concluded that the differential thermal desorption nature of the Joule heating thermal desorption and direct analysis in real time platform indicated efficient desorption and detection of the both inorganic and organic explosive mixtures and with each desorbing at its respective optimal temperature.

Swider (13) reported optimizing Accu Time-of-Flight/Direct Analysis in Real Time for Explosive Residue Analysis with the use of a direct analysis in real time (DART) mass spectrometer (MS) instrument was developed for 22 compounds of organic explosive residues to furnish a guide for DART-MS users to get rapid screening of explosive compounds. Samples were tested as neat solutions and sequential dilutions to know optimal instrument conditions and minimum concentration detection limit. In the negative ion mode most compounds were ameliorated to 250°C and several compounds by the addition of a chloride dopant from methylene chloride (amino-dinitrotoluenes, RDX, EGDN, and PETN). In the positive ion mode (TEGDN, DEGDN, HNS, and DMNB) some compounds were found more sensitive. Mixtures of compounds under study could be detected using clean room wipes, directly from their surfaces and subsequent extractions. According to author Compound in mixtures were clearly identified in soil and swipes of spiked surfaces. The instrument proved its merit in the detection of pg/µL solutions for most of the compounds and among the substrates.

Forensic analysis of black powders and their substitutes, directly from wipe-based sample collections, was demonstrated by Forbes and Verkouteren (14) using infrared thermal desorption coupled with DART-MS. Authors described that discrete 15 s heating ramps were generated, creating a thermal desorption profile that desorbed organic and semi volatile inorganic compounds at lower temperatures range i.e.250 to 400 °C and non-volatile inorganic oxidizers at high temperatures ranging from 450to 550 °C. The common inorganic components of black powders like Sulphur and potassium nitrate Sulphur and potassium nitrate and the dicyandiamide, sodium benzoate , guanidine nitrate ascorbic acid, and potassium per chlorate Using polytetrafluoroethylene-coated fibreglass collection wipes with no additional sample preparation organic and inorganic both types of components of black powder were identified. Authors reported that IRTD-DART-MS allowed the direct detection of intact inorganic salt species [$KClO_4$+NO_3] nitrate adducts) and larger clusters. The larger ion distributions which is generated by complex mixtures were differentiated utilizing principal component analysis of the mass spectra obtained at two points during the thermal desorption profile), additionally at high in-source collision-induced dissociation. The principal component analysis framework developed by the examination of the two black powders and five black powder substitutes used to classify samples obtained from a commercial firecracker. Combination of IRTD-DART-MS and multivariate statistics illustrated the significant utility for analysis of trace fuel-oxidizer mixtures

Conclusion

Forensics community is facing problems due to case backlogs, difficulties in analyzing trace evidence, different kinds of cases, unknown chemical compounds found at crime scene as well as in handling of upcoming technologies. More over numerous challenges are often encountered during the collection and analyzing the physical evidence at the explosion crime scene. Generally these evidences tend to blend into the background therefore collection process become tedious and difficult. To overcome with these complications efforts have been made at different levels by the forensic scientists occasionally. In the search the forensic scientists are pursuing the application of ambient ionization mass spectrometry and more especially DART-MS, for a wide range of applications. The above review pointing methodologies and researches demonstrating the use of DART-MS for forensically relevant samples specifically post blast explosive residues. Though a broad research base for forensic applications of DART-MS exists, there are still a number of areas left that require increased attention for the development of this method and to enhance its potential and significant utility.

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