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REVIEW ARTICLE

DART-MS: A Potential Ambient Ionisation Strategy That Revolutionises the Mass Spectroscopic Applications

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DART-MS: A Potential Ambient Ionisation Strategy That Revolutionises the Mass Spectroscopic Applications

SUMMARY

Direct Analysis in Real Time Mass Spectrometry (DART-MS), a potential ambient ionisation methodology revolutionises the applications of mass spectroscopy by being a swift and non-destructive procedure that can be applied for a wide range of samples. This review details the ionisation methodology, new developments with respect to the instrumentation, overview of the applications and the wide variety of sampling tools. A systematic review of the recent literature that uses DART-MS for the research study spanning 2020 to 2025 shows the widespread applications of DART-MS covering therapeutic drugs, drugs of abuse, adulteration in food, categorisation of microorganisms, species authentication, forensic samples, environmental pollutants, toy safety etc. The structured presentation of findings acts as a valuable resource for researchers and industry professionals, promoting a deeper comprehension of this developing analytical tool and its increasing importance in contemporary scientific inquiries.

Keywords: *DART-MS, ambient-ionisation, mass spectroscopy, jumpShot, forensic, Penning, Helium, OpenSpot.*

DART-MS: Kütle Spektroskopi Uygulamalarını Devrimleştiren Potansiyel Bir Ortam İyonizasyon Stratejisi

ÖZ

Gerçek Zamanlı Kütle Spektrometresinde Doğrudan Analiz (DART-MS), potansiyel bir ortam iyonlaştırma yöntemi olarak, hızlı ve tahrip edici olmayan bir işlem olması sayesinde kütle spektroskopisinin uygulamalarını devrim niteliğinde değiştiriyor ve geniş bir örnek yelpazesi için uygulanabiliyor. Bu derleme, iyonizasyon yöntemini, cihazlarla ilgili yeni gelişmeleri, uygulamalara genel bir bakışı ve çeşitli örnek alma araçlarını detaylandırıyor. 2020-2025 yılları arasında DART-MS kullanılarak yapılan araştırmaları kapsayan son literatürün sistematik bir incelemesi, terapötik ilaçlar, kötüye kullanım ilaçları, gıdalardaki katkı maddeleri, mikroorganizmaların sınıflandırılması, tür doğrulaması, adli örnekler, çevresel kirleticiler, oyuncak güvenliği vb. konuları kapsayan DART-MS'in yaygın uygulamalarını göstermektedir. Bulguların yapılandırılmış sunumu, araştırmacılar ve sektör profesyonelleri için değerli bir kaynak olarak hizmet eder ve bu gelişen analitik aracın ve çağdaş bilimsel araştırmalardaki artan öneminin daha derin anlaşılmasını teşvik eder.

Anahtar Kelimeler: *DART-MS, ortam iyonizasyonu, kütle spektroskopisi, jumpShot, adli, Penning, Helyum, OpenSpot.*

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INTRODUCTION

The development of the ambient ionization technique can be regarded as a remarkable step in mass spectroscopy. The new ionisation process does not necessitate any sample pretreatment and can even function in open air, facilitating the surface sampling of any sized or shaped materials, and is possible for the materials in their native state. Another major breakthrough is the sampling of several samples in less time, facilitating high-throughput screening (Ackerman & Noonan, 2009; Gupta & Samal, 2022). There are some novel ambient ionisation processes available, in which Direct Analysis in Real Time Mass Spectrometry (DART-MS) was invented and commercialised first. It can be regarded as a revolutionary development in mass spectrometry with respect to ionisation as it can literally convert any substance in its native form at atmospheric pressure to ions that can be analysed by mass spectroscopy (MS) facilitating the mass spectra in seconds by simply inserting it in the void between DART device and MS. Since any hazardous solvents are not used in any step, it can be rightly regarded as a green analytical technique. Currently the use of green analytical techniques is preferred in order to reduce environmental pollution (Mathew & Varma 2022). Normally, sample processing is a tedious and sluggish step and it limits the substrates for analysis and in DART this issue is overcome. DART resulted from the efforts of Laramee and Cody in an attempt to devise a safer alternative to work under atmospheric pressure, and hence capable of replacing the hazardous radioactive sources present in the chemical weapon detectors. The pioneering discovery, which happened between late 2002 and early 2003, led to a US patent in 2003 (Sisco et al., 2020). There is yet another ambient ionisation method named desorption electrospray ionization (DESI), which permits direct sample analysis with zero sample processing. DESI works with a liquid spray, whereas DART uses a dry gas stream with excited state species (Cody et al., 2005). Being an ambient ionisation strategy, it has a wide range of applications in food adulteration, forensics, and the detection of drug molecules, narcotics, etc. The beauty of this technology lies in its flexibility regarding the sample state, as it enables the sampling of solid, liquid, or gaseous states without any sample pretreatment or preparation (Harris et al., 2012). Because of its adaptability, DART-MS can be used in a wide range of scientific fields. Interestingly, for the years 2020–2025, there are no studies that provide insight into the latest analytical applications. Therefore, in order to close a major gap in the literature, the authors have tried to address the technology, new applications, and instrumentation developments in this study. Direct analysis, a revolutionary ionisation process, and mass spectroscopy are all uniquely combined in DART-MS, a superior analytical chemistry technique. A thorough and effective analysis is made possible by this combination (Figure 1.).

How did it derive the name DART?

Direct **A**nalysis (No sample preparation) + **R**eal **T**ime (instantaneous result with no time lag) = **DART** (a versatile ionisation strategy)

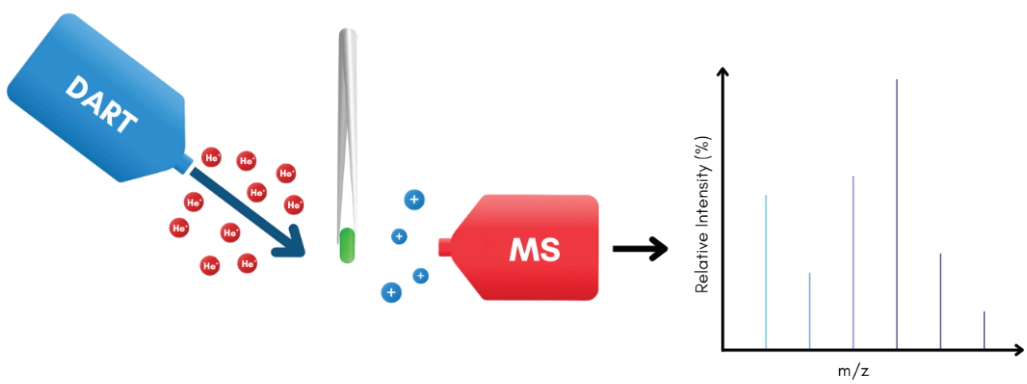


Figure 1. Overview of DART-MS process

Salient features of DART-MS

- Good mass resolution instilled mass spectra achieved in real time
- Sample feasibility:
  - Any size, shape or geometry.
  - Possible to analyse gas, solid, liquid or even live organism.
  - Direct surface analysis for analytes without any sample preparation like solvent extraction or wiping
- No need of any interface between DART and MS
- First Ambient ionisation method discovered. (functions at atmospheric pressure and does not need any specialised feature)
- Powerful problem-solving tool
- Wide applicability- forensics, material analysis, environmental testing etc.
- No carry over with rapid and noncontact analysis of material
- Depends on the reactions of reagent molecules as electronic or vibronic excited species with polar or non-polar analytes.
- Very fast response providing results in real time, a key requisite for high throughput screening.

Formation and functioning of metastable reagent gas stream

There is extensive research on best practices and limitations for various attributes, as well as an understanding the actual mechanism in the ionization process, which led to the Penning ionization of water as the predominant process (Cody et al., 2005). Nitrogen, too, can be used as the ionization gas, and its mechanism in ionization is also widely studied. There is a considerable amount of research that aims to elucidate the ionization process, as well as the sample positioning and introduction to the analytical characteristics (Domin, 2014; Dong, 2017; Harris et al., 2012; McEwen & Larsen, 2009). Penning ionization process derived the name from a Dutch physicist, Frans Michel Penning, who researched the electric discharge on inert gases at Eindhoven in Philips Natuurkundig Laboratorium, where he measured the electron liberation from metals due to positive ions and metastable atoms (Penning, 1927). Penning ionization, a type of chemi-ionization, involves reactions between neutral atoms or molecules (Arango et al., 2006). The successful ionisation through DART is facilitated by the specific design of the unit that helps one to understand the ionisation mechanism clearly. The reagent gas is energized to an excited state of long life (electronic/vibronic state).

(i) An auxiliary heating device heats the gas to elevate its temperature, and

(ii) In the ionization zone, the analyte ions in the gaseous state are created by the ambient ionization of air from the metastable reagent gas (Dong, 2017).

In the atmospheric pressure region of the DART source, the reactant ions interact with the sample, yielding the characteristic sample ions that are directed to the atmospheric pressure interface (API) of the MS. The ions are formed in DART due to the ambient air–chemical reactivity triggered by the generation of a metastable gas. Hence, the ionization process can be rightly regarded as a gas-phase ionization method. Here, the ions are generated from the sample based on the reactions of the molecules vaporized with the excited metastable reagent (Dong, 2017).

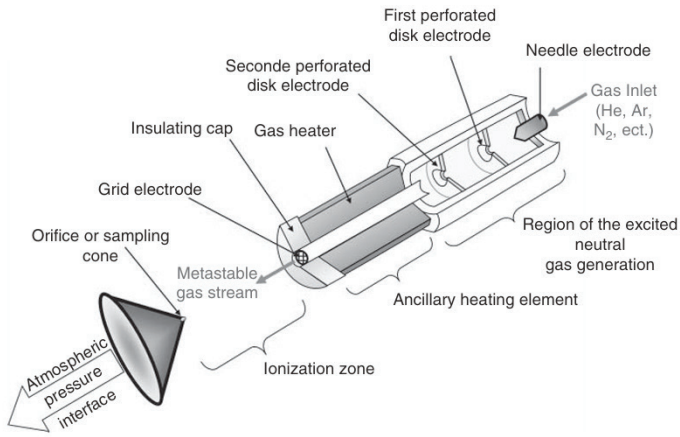


Figure 2. DART device (Dong, 2017)

The DART source is a multichambered tube as shown in (Figure 2.) in which N_2 or He is converted into electronic or vibrationally excited species, and the resulting metastable He atoms or N_2 molecules serve as the reagent gases in DART (Cody et al., 2005). Initially, the gas is sent to a discharge chamber fitted with a needle electrode and a first perforated disc electrode (Cody et al., 2005). The gas reaches the chamber through the needle, and the needle electrode is kept at a positive potential. (typically, +1 to +5 kV) with respect to the counter electrode (grounded first perforated electrode). The electrical discharge can be regarded as a corona-to-glow (C-G) discharge regime. The high voltage values correspond to the corona discharge process, whereas the discharge currents (a few milliamperes) can be compared to what occurs in a glow discharge regime (Sisco et al., 2020). Due to the strong density of electrons emitted in the intense electric field, the gas is ionized, creating a plasma consisting of ions, electrons, and electronically/vibronically excited species (Cody et al., 2005; Dong, 2017). Since He is the most widely used gas in DART, let us see the reagent gas production process. The electrical discharge generates helium ions and thermal electrons. In the DART source, the higher pressure and current density reduce the charge separation and lead to the readdition of the radical cation He+• and the emitted thermal electrons, resulting in the generation of metastable helium atoms (denoted as He* or He2^{3}S) with a long-life species. By a similar process, the corresponding neutral metastable species can be generated with argon or nitrogen. The generated excited species will show variation with respect to ionization energy (IE), internal energy (Eint), and the type of excited states (Dong, 2017). The emerging gas stream from the DART source contains metastable species, as well as unwanted charged species. Therefore, before reaching the ambient atmosphere, this stream must be purified for which it is sent to the second chamber fitted with a second perforated disc electrode (Cody et al., 2005). By means of a positive potential at the second perforated electrode, the cations are removed from the gas stream in positive ion mode, whereas negative potential need to be applied to remove anions when the operation mode is negative (Dong, 2017). Now the gas stream is directed to the third region where a grid electrode is present (another perforated electrode) which is also fitted with a heating element that can raise the gas temp to a maximum value of 250°C. The grid electrode can have a positive or negative potential, depending on the requirement, and the value ranges between 250V and ±700V. The grid electrode functions as an ion repeller and removes ions with the opposite polarity and stops ion-ion readdition, as it may weaken the signal. This last step is very crucial as it permits only the suitable ions for detection (Cody et al., 2005). The potentials of the second and third perforated electrodes (grid electrodes) were biased to

positive and negative potentials, respectively, for the detection of positive and negative ions. The electrode polarities were critical, with typical values of 100 V and 250 V, respectively (Cody et al., 2005). The typical gas flow rate is in the range of 1.5 L/min to 3.0 L/min. By means of a "pulsed" DART technique, a new development in DART-MS allows intermittent gas flow that can minimise the gas consumption up to 95% and improve the efficiency (Sisco & Forbes, 2021). A hot gas stream of neutral atoms with a long half-life in the excited state finally exits from the third perforated electrode, that can desorb the sample as ions in their vapour state. It is regarded as an essential part of the DART ionisation process as it can guarantee the desorption of analyte molecules from either liquid, solid, or vapour phase materials. The DART gas flow can be directed towards the MS orifice or reflected off a sample surface and subsequently directed to the MS orifice (Cody et al., 2005). The direction and distance of the DART source can be varied with respect to the API orifice of the mass spectrometer. It can be used in transmission mode for an on-axis configuration or in desorption mode, where the DART stream flows tangentially to the surface of a sample introduced into the ionization region (Cody et al., 2005). The distance "Insulator cap–Sample–API Orifice" can vary in a range of 5–30 mm, though the ions could be detected even when the said distance was 1 m (Dong, 2017). The correct positioning, distance, or angle of DART with respect to the sample surface and the mass spectrometer are flexible, though optimum geometries may exist for specific applications. The DART position was adjustable on an x, y, z stage over a wide range of angles and distances (Cody et al., 2005; Gupta & Samal, 2022)

Ionization mechanisms in positive DART

In positive mode, the ions are generated using a similar strategy to that of APCI (atmospheric pressure chemical ionisation), with two major exceptions. The initial reagent ion production in APCI is due to corona discharge, whereas it is due to Penning ionisation in DART. Secondly, the nature or the composition of the surrounding atmosphere will vary: In APCI, it is N_2 gas as it is used as an ancillary gas, whereas in DART, moist ambient air made of nitrogen (N_2), oxygen (O_2), and water (H_2O), which is present in the area of ionisation (Dong, 2017).

Though we can use neon, argon or nitrogen, Helium is the most effective DART gas because its internal energy in the metastable state is the highest (IE=19.8 eV). Penning ionisation reaction undergoes between metastable He, denoted as He(2^3S) and the analyte and can be written as

$He(2^3S) + M \rightarrow M^{+\bullet} + He(11S) + 1e^-$ Penning ionization (Dong, 2017).

The basic principle behind DART-MS is the generation of heated metastable gas atoms that can desorb and ionise the analyte of interest, and the generated ions are suitable candidates for further MS analysis (Sisco & Forbes, 2021). Helium is the most preferred gas, as its metastable state has enough energy to ionise water in the atmosphere, which can, in the subsequent steps, create charged water clusters. The charged water clusters can ionise the sample molecules in the positive DART mode. The related chemical equations are presented in Equations 1-4 (Sisco & Forbes, 2021).

$$He^* + H_2O \rightarrow He + H_2O^{+\cdot} + e \quad (1)$$

$$H_2O^{+\cdot} + H_2O \rightarrow H_3O^+ + OH^{\cdot} \quad (2)$$

$$H_3O^+ + nH_2O \rightarrow [(H_2O)_{n+1}+H]^+ \quad (3)$$

$$M + [(H_2O)_{n+1}+H]^+ \rightarrow [M+H]^+ + (H2O)_{n+1} \quad (4)$$

The energy of the metastable states of N_2, Ar or air are less hence they are not capable to directly ionise H_2O and hence not much preferred over He. The direct ionization of the analyte, or dopant, is needed and is found to be less efficient (Equation 5 and 6) (Dong, 2017). On top, the use of air may produce ozone that may have harmful effects on the system hardware (Sisco & Forbes, 2021).

$$N_2^* + M \rightarrow N_2 + M^{+\cdot} + e \quad (5)$$

$$M^{+\cdot} + M \rightarrow [M - H]^{\cdot} + [M+H]^+ \quad (6)$$

In brief, the hydronium ion and the charged water clusters generated are the predominant ionising species in positive DART which converts the analyte species M to $[M+H]^+$ ion. Radical cation M+• also can be generated from an analyte M by charge exchange reactions between reagent ions G+• and the molecule M as shown in Equation 7.

$$G^{+\bullet} + M \rightarrow M^{+\bullet} + G \quad (7)$$

Ionisation mechanisms in negative DART

The DART ionisation process can also be performed in negative ion mode, although very few works have been reported. The generated negative ions include the radical anions M−• and the deprotonated molecules [M−H]− from the analyte species, M. In negative ion mode, also, the metastable helium species He(2^3S) or He*) are generated by the needle discharge electrode occurring in the first part of the DART source. The glow-to-corona discharge regime also yields anions and electrons that must be removed by applying a negative voltage to the second perforated disk electrode (e.g.,- 100V). The grid electrode must be maintained at a negative potential (typically −250V), and upon heating, the hot metastable gas stream emerges, containing negative ions that are directed toward the MS orifice. In front of the insulating cap, the electrons are also retained (Dong, 2017).

DART MS instruments

DART was invented in 2003 at the MS Applications Lab of JEOL USA, Inc., for the JEOL AccuTOF series of mass spectrometers, ensuring optimal performance with this combination. It enables real-time sample analysis by simply inserting any sample, regardless of size or shape, into the DART ion source, eliminating the need for sample preparation and saving time. This results in accurate mass spectra with the best mass resolution in real-time. It can even handle dirty samples that a conventional process cannot. When used with AccuTOF, it does not require any interface, as it operates through a simple API and a robust vacuum pumping system, which also enables zero carryover between analyses, even for dirty or sticky materials. The AccuTOF™-DART® 4G is an atmospheric pressure ionization, high-resolution time-of-flight mass spectrometer (API-HRTOFMS). This versatile instrument offers solutions for various problems and can operate alternately with atmospheric and ambient ionisation sources. One can rapidly obtain high-resolution mass spectra of any sample by positioning it as such, in the gap between the DART source and the MS inlet. Sampled materials can vary from solutions of synthetic reactions, crude drugs, tablets, ink or stain, polymers, TLC plates and so on. The combination of advanced TOF instruments with a DART ion source, which functions with zero sample preparation in ambient conditions, revolutionized the scope of mass spectroscopy. The close integration of the unique ionization source with TOF precludes the use of any pump, flanges, or any interface device. The third-generation AccuTOF-DART 4G system is an "Ambient Ionisation Toolbox™" that allows the analyst to choose ionisation methods that are best matched to the samples to be analysed. The DART ion source can be operated in several different modes on the AccuTOF-DART 4G, and a wide range of ambient ionization methods can be carried out without removing the DART ion source 13 (JEOL USA, 2022).

There are three advanced instruments namely, DART OS, DART JumpShot® and DART JumpShot $^{@HTS}$ and are detailed below and picturised in (Figure 3.). DART-OS implies DART with the OpenSpot module, which permits fast and user-friendly analysis where ionization occurs in an enclosed area and precludes any sample contamination.

Figure 3. Advanced DART MS instruments (Bruker Daltonics)

This is very useful for a synthetic chemist who needs to analyse the sample more frequently. Unlike traditional methods, DART-OS eliminates the need for solvents or vials. With no moving parts and simplified hardware, it easily mounts to any LC/MS system, enabling quick transitions to an open ionisation region when needed. It also supports dopant-based ionisation and derivatisation, making it highly adaptable for complex analyses. DART-OS simplifies the ovearall process in such a way, it is accessible to all users with a chromatography-free approach to analyse a wide range of compounds. It features fast installation, minimal sample preparation, and rapid results, making it ideal for applications that demand immediate answers (Bruker Daltonics). DART-OS works in simple steps, yielding the mass spectra in seconds. Specialized OpenSpot® cards are available to apply the sample in the designated area. When the card is inserted into the system, the heated carrier gas passes through the sample, and the sample is desorbed and ionised. The card is discarded after analysis (Bruker Daltonics).

DART JumpShot® is an ultra-fast, automated version of DART-MS that is very suitable for high-throughput analysis with good sensitivity at reduced operational charges. It uses a QuickStrip® wire mesh grid that can analyse 12 samples within 3 seconds, and in multiple rail automation mode, it can deal with 96 or 384 samples at a time (Bruker Daltonics). It has some inherent advantages, such as automation and speed, which ensure faster sample analysis compared to standard DART. It reduces helium gas consumption by 90-95%. As it has less background noise, it provides a higher signal-to-noise ratio and improves the sensitivity. Regular data processing is improved by sharper, more distinct peaks. Additionally, it improves precision by lowering interference from surrounding ions. JumpShot® uses pulsed gas technology in place of a continuous gas flow, guaranteeing focused ionisation of every sample in one to two seconds. This approach speeds up analysis by processing samples more efficiently, lowers gas usage, cutting down costs and environmental impact, and enhances data quality by reducing unwanted background noise (Bruker Daltonics).

DART JumpShot® HTS is a fully automated version with the highest efficient DART-MS device for high-throughput screening, and one can analyse large volumes of samples at a faster rate. The analyst can save time while maintaining accuracy and reliability in the mass spectra. It uses pulsed gas technology that enables cutting out the background noise and increases the sample ionisation (Bruker Daltonics). Analyses 96 samples in 6 minutes and 384 samples in just 22 minutes, providing the fastest throughput. It simplifies sample handling and analysis as it is an automated version. Sharper peaks and less background noise improve detection accuracy. It makes high-throughput mass spectrometry accessible to all users and is hence regarded as user-friendly. For the analysis, Automated pipetting transfers nanoliter volumes onto a QuickStrip® HT Wire Mesh Screen from a 96 or 384-well plate. The screen is placed into the JumpShot® HTS interface, where an automated rail system moves from

sample to sample for rapid analysis (Bruker Daltonics). It is used in forensics for automated analysis of seized drugs, including traditional drugs, New Psychoactive Substances, steroids, and supplements. In food & Beverages, it is helpful to screen the contaminants like pesticides and packaging additives. Trace detection of complex matrices for environmental monitoring can also be done. Rapid QC and inspection of materials, including microplastics, streamlined analysis for drug discovery and quality assurance, and quick detection of explosives and other hazardous substances are other areas of application of DART JumpShot® HTS (Bruker Daltonics).

VARIEGATED SAMPLER DEVICES FOR DART-MS

A wide variety of sampler devices are available for DART-MS, including Dip-it sampler, screening module, metal screen, plate holder system, TLC or HPTLC plates, 96-well plates, capillary electrophoresis (Bai et al., 2012; Chang et al., 2013; Guo et al., 2014; Kim et al., 2010; Krechmer et al., 2011; Morlock & Ueda, 2007; Vaclavik et al., 2009) etc. The picture of some selected ones is shown in (Figure 4.).

IonSense has innovatively designed the VAPUR interface, a crucial component that carries ions from the DART ion source to the MS orifice. This interface, equipped with a diaphragm inlet pump, maintains a reduced vacuum in the VAPUR interface chamber, ensuring efficient ion transfer (Dong, 2017). The DIP-it sampler, with a glass tip for dipping into the sample, is a versatile sampler and for medium sample size, it can be kept on a linear rail (LR) with 12 sample sets (MartínezVillalba et al., 2013; Zachariasova et al., 2010). The analyte solution can be held onto the glassy tip, and the sample-loaded tips are secured on the LR, which can move at an optimised pace. AutoDART-96 is used for high-throughput sampling which is an autosampler device provided with a robotic arm that can automatically hold the DIP-it sampler and place it in a 96-well plate to collect the liquids for analysis. It is very adaptable for DART-OS and DART JumpShot® (Cajka et al., 2013; Chernetsova et al., 2012; Dong, 2017; Novotná et al., 2012; Vaclavik et al., 2010).

The Auto DART HTC PAL autosampler (Leap Technologies, USA) was created to improve sample placement reproducibility (Sparkman, 1996). It offers high analytical throughput, accurate sample positioning inside the ionisation area, and compatibility with interchangeable DIP-It glass tips. In contrast, the reasonably priced DIP-It holders, which come in one-tip and twelve-tip varieties, increase placement precision as compared to manual handling. With a larger sample input, this probe's twelve coils of 0.12 mm Ni-Cr resistance wire wound around a syringe needle increase its surface area (Jeckelmann & Haefliger, 2010).

For surface sampling, porous samplers such as fabric, swab, filter paper, etc., are used. E.g., perfumes on cloth (Pérez et al., 2010), and the pesticide remnants on fruits or vegetables (Crawford & Musselman, 2012; Edison et al., 2011b; Kern et al., 2014). Multiple sample holders can be kept in line, in the void between the DART device and the MS orifice and passed through by the helium gas stream in a perpendicular direction to the axis (Dong, 2017).

Metal mesh is a suitable sample holder for liquids such as fruit juice or extract with increased sample load and available in three grades. Different types are available (Dong, 2017). There is another set made up of non-conducting material with a medium throughput of 10 sample loads, called transmission mode DART (TM-DART) (Farré et al., 2013; Haefliger & Jeckelmann, 2007). Another medium-throughput metal screen variant comprises heat-conducting material called thermally assisted DART (TA-DART). In TA-DART, a heated metallic screen is used as a sample holder, enhancing the vaporisation rate of molecules. This technique is used for liquid chemical standards, chemicals in solution, and powders, and it is found to drastically reduce the time requirement (Krechmer et al., 2011). Direct heating facilitates the vaporisation of liquid analytes, and one can modulate the process by varying the current input. E.g., swift wipe off of single

drugs Vs graded wipe off of mixtures (Dong, 2017). IonSense developed the high-throughput XZ-TM-DART sampler that can handle 96 samples within 20 minutes is ideal for high-volume sample analysis. The transmission-mode DART (TM-DART) sampling strategy, combined with the fabricated sample holder, wherein the rapid exposure of the samples to the metastable gas stream yields efficient ion desorption onto the MS orifice (Sisco & Forbes, 2021; Vaclavik et al., 2013). Having 96 or 384-well plates it is provided with auto-pipettors and robotic sample pipetting systems to deliver the correct volume of analyte into each well.

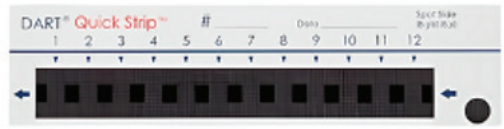
Another sampler by ionsense is the Open Spot cards (IonSense), with an inbuilt metallic grid coupled with the ID-CUBE ion source with one sample load (Chernetsova et al., 2012). Thermal desorption rate is enhanced by means of an electric current to the metal grid to desorb the analytes to the MS orifice, as in TA-DART, within 20s (Dong, 2017). OpenSpot® sample cards are made up of wire mesh and can retain only a single sample, such as powder or liquids, spotted at the center of the screen. These card samplers are effectively used with the DART-OS interface. QuickStrip™ sample cards for DART JumpShot® are useful for automatic sampling of powders and liquids. Each card is provided with 12 sample slots where each sample can be spotted onto the wire mesh screen prior to loading into the DART interface (Dong, 2017).

TLC or HPTLC plate or a 96-well plate (3D) can permit the in-situ analysis of sample after chromatographic separation. TLC is the best less expensive tool for the separation of natural products and for the detection, one can adopt TLC-DART-MS (Dong, 2017). This method is used for the separation and screening of curcumin in Turmeric by DART-MS (Guo et al., 2014) wherein the extract was separated on a TLC plate, positioned the separated curcumin bands by viewing under UV light (365nm) and was directly exposed to the metastable helium gas stream for DART analysis. On comparing with the simple DART-MS, TLC/DART-MS yields better results, especially for complex mixtures (Dong, 2017; Zhang et al., 2012). For low molecular weight species, a novel plasma-assisted multi wavelength laser desorption ionisation technique (PAMLDI) is used in collaboration with TLC/DART-MS (Dong, 2017; Zhang et al., 2012).

The tweezers (Rothenbacher & Schwack, 2010; Schrage et al., 2013; Vail et al., 2007) or fingers (Edison et al., 2011a; 2011b) can hold the material for the surface sampling. Solid materials like tablets can also be handled with the tweezer holder for one or the tablet carrier for 10 tablets (Self & Wu, 2012). A novel confined DART (cDART) device is used for gaseous analytes by means of a Tee-shaped interface between the DART ion source and the API interface (Li, 2012).

A reported research work for the fast analysis of numerous phytohormones in fruit juice is based on single-drop liquid–liquid–liquid microextraction (SD-LLLME) along with DART-MS. Proper optimisation of the extraction process and operating parameters yields better extraction efficiencies and detection sensitivities for SD-LLLME-DART-MS (Bai et al., 2012; Dong, 2017). SPE-it™ tips are formed from SPME fibres and function as a SPME device, like a micropipette, isolating the analyte from the aqueous solution. It is best with DART-OS and DART JumpShot® for automated analyses and for liquids. Each card is provided with 12 sample slots where each sample can be spotted onto the wire mesh screen and finally loaded into the DART interface (Dong, 2017).

a) OpenSpot® sample cards

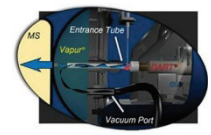


b) QuickStrip™ sample cards

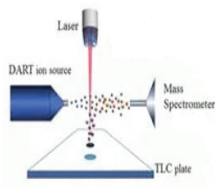
c) QuickStrip™ HTS sample cards

d) DIP-it sampler

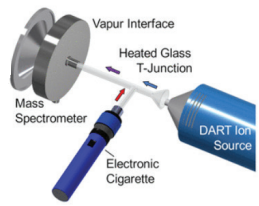
e) SPE-it™ tips



f) VAPUR



g) TLC plate



h) Tee junction

Figure 4. Various samplers for DART-MS

MAJOR RESEARCH AREAS USING DART-MS DURING 2020-2025

Technology is advancing, and so also the adulteration and other evil practices, such as the usage of illicit drugs, chemical weapons, etc. Living beings are exposed to toxic materials knowingly or unknowingly; hence, it is essential to monitor this to make the world a better place to live in. This is possible through the on-time screening of the various sources of contamination or adulteration. Here, we need to value the utility of DART-MS for its fast analysis with zero sample preparation. A thorough exploration of the published literature spanning 2020-2025 covers its use for various sources of toxic products or residual solvents in PPE, toys, nail paints, and the atmosphere, among others. This technology can be used for authenticity testing, adulteration testing, or microbial infestation detection in wine, saffron, animal feed, cereals, and Cocca products, among others. Another area is the screening for designer drugs and illicit drugs that facilitates the forensic database. E-cigars also may contain illegal drugs that can be identified. One can classify the plant species based on ML-assisted chemical fingerprinting, which is preferred as it does not harm the plants. Another needed area is the screening of organophosphate nerve agents used as chemical weapons (Qu et al., 2023) and nitrosamines in drugs. Based on chemical profiling, the source of poultry

meat can be categorised. The presence of brominated flame retardants in food packaging materials and PFAS in the environment can be monitored. Microbial species can be classified with respect to lethality based on the volatile organic compound signature, and the use of machine learning further simplifies the process. Trace-level detection of drugs or their metabolites in biological fluids and drug residues in animal fat is achievable. DART-MS is a boon to analysts as it can detect contaminants in everyday products or the environment. These research areas are illustrated in (Figure 5.).

Figure 5. Recent applications of DART-MS

1. Forensic application

DART-MS has a prominent role in forensic science where scientific principles and methods are adopted to support the decision making in order to implement the civil and criminal law.

Intact explosives

Estevanes et al. (2024) investigated the combined use of confocal Raman microscopy and DART-MS for analysing intact explosives. The integration of molecular fingerprinting with rapid chemical profiling demonstrates innovative, reliable approaches. Highlighting this synergy can inspire confidence in the potential of advanced, dependable forensic techniques for security applications.

Designer drug screening

Couch et al. (2023) devised a DART-MS based method for designer drug screening. The research evaluates the utility of the NIST DART-MS Forensics Database and Data Interpretation Tool for screening designer drugs with alternative mass spectrometry instruments. The database facilitates the identification of emerging synthetic drugs by comparing spectral data with known references. The study assesses its compatibility with different MS platforms, highlighting its strengths and limitations. Results suggest that the tool enhances forensic drug analysis by improving accuracy and efficiency; however, variations in instrumentation may impact identification reliability, necessitating further optimization.

Illicit substances

Song et al. (2020) investigated the application of N_2 DART-TOFMS for rapid screening of forensic drugs. The method provides fast, accurate, and high-throughput detection of illicit substances with zero sample preparation. Using nitrogen as the ionization gas enhances spectral clarity and reduces background noise, improving drug identification. The study demonstrates the potential of N_2 DART-TOFMS as an efficient tool for forensic drug analysis, offering a reliable alternative to traditional techniques.

Multi-elemental sample analysis

Moorthy & Sisco (2021) developed a multi-elemental sample analysis with DARTMS. This study presents a new library-search algorithm designed to improve the analysis of mixtures with DART-MS. The algorithm enhances the identification of multiple compounds within complex samples by optimizing spectral matching and reducing false positives. It improves the accuracy of chemical identification by considering ion intensity patterns and fragmentation behaviour. The approach demonstrates superior performance in analysing mixtures compared to conventional methods, making it a valuable tool for forensic, pharmaceutical, and environmental applications.

Confiscated drugs

Cooman et al. (2021) developed dual techniques based on Portable Raman spectroscopy and DART-MS for the screening of confiscated drugs. Seized drugs can be effectively screened faster with DART-MS and Raman spectroscopy, and the techniques are complementary for the screening process of illicit drugs, as they facilitate the drug detection with improved specificity and sensitivity. The dual techniques are valuable in forensic applications and constabulary in real-time drug analysis.

Electronic cigarette aerosols and spike drugs

Forbes and Krauss (2021) used DART-MS for the rapid analysis of electronic cigarette aerosols and spiked drugs with respect to the chemical content. The method enables the direct detection of nicotine, flavouring compounds, and illicit substances in e-cigarette vapours without extensive sample preparation. The study highlights the sensitivity and efficiency of confined DART-MS in identifying harmful or unauthorized chemicals in vaping products, offering a fast and reliable tool for regulatory and forensic applications.

Cannabinoids

Chambers and Musah (2022) developed a fast estimation process for cannabinoid-infused edible stuff, personal-care products and *Cannabis sativa*

hemp plant material employing DART-HRMS. It is a good tool for screening the presence of cannabinoids in personal care products, edible items, or Cannabis sativa. It has the added advantage of zero sample preparation, as well as rapidity, etc. It is an effective means to detect cannabinoids in various substances, QC, compliance testing and law enforcement investigations. DART-HRMS effectively differentiates cannabinoids in complex matrices, providing a fast and reliable triage approach for regulatory and forensic applications. The findings highlight its potential for identifying cannabinoids in diverse products, aiding quality control, compliance testing, and law enforcement investigations.

Seized drugs

Sisco et al. (2022a) developed a DART-MS method for the qualitative analysis of seized drugs with an internal standard. This study aims to enhance the analytical results concerning the seized drugs by DART-MS with the aid of an internal standard. The internal standard enhances reproducibility, accuracy, and reliability in detecting illicit substances by compensating for variations in ionization efficiency and sample positioning. The study evaluates different compounds as potential internal standards, determining their capability in stabilizing signal intensity. The results demonstrate the effectiveness of an internal standard in improving the qualitative drug profiling, making DART-MS a sturdier technique for forensic drug screening.

Sisco et al. (2022b) developed a validation template based on DART-MS for the qualitative seized drugs analysis. The validated methodology helps one to perform the screening of seized drugs. It outlines key parameters such as accuracy, reproducibility, specificity, and sensitivity, ensuring reliable identification of controlled substances. The proposed framework helps standardize DART-MS for forensic applications, enhancing its credibility in drug enforcement. By comparing results with established techniques, the study confirms DART-MS as a quick and effective screening tool for seized drug analysis.

2. Volatile compounds

Volatile species

Machado et al. (2025) used DART-HRMS for identifying volatile species of Ruthenium and Osmium, employing N_2DART-HRMS to detect unknown volatile carbonyl compounds produced by UV photolysis of formic acid-based media.

C_6 aldehydes

Bates and Sacks (2024) researched the use of DART-MS for the quick analysis of C_6 Aldehydes. This study presents a rapid method for analysing C_6 aldehydes using Solid-Phase Microextraction Sheets (SPMESH) in conjunction with DART-MS. The approach enhances sensitivity, minimizes sample preparation, and enables real-time detection of volatile compounds. The method is effective for assessing food quality, environmental monitoring, and fragrance analysis. Validation experiments confirm its accuracy and reproducibility, demonstrating its potential for fast, high-throughput analysis of C_6 aldehydes in complex sample matrices.

Volatile organic compound (VOC) signatures of microbes

Arora et al. (2022) developed discriminative volatile Organic Compound signatures from microbes using SPME-DART-MS, clubbed with Machine Learning Approaches to identify the species. Machine learning (ML) methods can be developed to identify fungi and bacteria based on the specific VOC signature of each organism using SPME-DART-MS. ML algorithms enable the differentiation of microbial species with reasonable accuracy, rapidity, non-invasiveness, etc. This development has applications in medical diagnosis, food safety, and environmental monitoring.

Volatile phenols from grapes

Rafson and Sacks (2021) extracted volatile phenols from grape juice by ımmersive sorbent sheet extraction (ISSE) followed by analysis using DART-MS. ISSE efficiently captures volatile compounds, enhanc-

ing their detection by DART-MS for quick and direct analysis. The approach provides high sensitivity, minimal sample preparation, and fast detection of phenolic compounds, which influence grape juice and wine quality. Hence, the extraction-detection methodology is very beneficial for QC testing and authentication in the wine and beverage industry.

VOC profiles of Fusarium species

Busman, et al. (2022) set up the VOC profiles of Fusarium species and used to generate a chemical fingerprint. Fusarium fungi produce mycotoxins, and there is species-specific variation. DART-MS can produce the chemical fingerprint of volatile organic compound (VOC) profiles of the mycotoxin, which can be used for species identification and categorization based on the risk potential, and hence it has application in the food industry, agriculture, mycology, etc.

Brominated flame retardants (BFRs) in soiled food contact materials

Paseiro-Cerrato et al. (2021) used DART-HRMS and GC-MS to identify Brominated flame retardants (BFRs) in soiled food contact materials with the aid of DART-HRMS and GC-MS. The study highlights the effectiveness of the former technique for rapid screening and the latter technique for confirmatory analysis. The findings indicate widespread contamination, raising concerns about potential human exposure to BFRs. The study underscores the need for stricter regulations and improved monitoring techniques to ensure food safety and consumer protection.

3. Sample authentication and adulteration and safety

Adulteration detection in saffron

Monaci et al. (2025) developed a fast adulteration detection process for saffron using DART–QQQ-MS. It helps to detect possible adulterants, such as turmeric and safflower, in saffron. It does not require any chromatographic separation and is a rapid process.

Coniferous species classification

Park et al. (2022) researched and developed ML algorithms using DART-TOF-MS data for Coniferous species that enable easy classification. Based on the chemical fingerprint of individual coniferous species prepared with DART-TOF-MS, machine learning algorithms are developed that help one categorize the species. It shows the non-destructive means to classify the species using the potential of DART-TOF-MS to prepare the data-driven models, facilitating a fast and accurate way of categorization. This approach has applications in forestry, conservation, and forensic sciences, ensuring proper species authentication and preventing illegal logging.

Screening of new psychoactive substances (NPS)

Hsu et al. (2024) developed a process for the fast Screening of New Psychoactive Substances using pDART-QqQ-MS. The authors developed a rapid and highly sensitive analytical methodology for NPS (new psychoactive substances, which are the functional/structural analogues of illicit drugs) using paper-loaded DART with QQQ-MS (pDART-QqQ-MS), enabling the analysis of these substances in a urine sample.

3. Pollutants, toxins

Toy safety

Yan et al. (2024) researched toy safety assessment with DART-MS. DART-MS was combined with differential mobility spectrometry (DMS), which enables post-ionization ion mobility separation, a crucial step for handling complex sample analysis by DART-MS. Primary aromatic amines are potentially hazardous chemicals that can be found in nail paint, toy products, plush toys, and bubble solutions, among other products.

Analysis of PFAS-toxins

Emmons et al. (2023) established a method based on SPME-DART-MS for the rapid analysis of PFAS. The researchers optimized the parameters using CCD for DART-MS characterization of polyfluoroalkyl substances (PFAS), a recent category of anthropogenic toxins derived from materials used in daily life.

Organic pollutants in atmosphere

West et al. (2023a) researched and developed a method for assessing pollutants in Organic Aerosol Mixtures using TPD-DART-HRMS. Experiments based on temperature-programmed desorption (TPD) coupled with DART-HRMS are used to identify and quantify the organic pollutants present in the atmospheric aerosols at ambient pressure, with zero sample preparation steps.

Thermal destruction of PFAS

West et al. (2023b) built a methodology to test the effectiveness of thermal destruction of PFAS by TD-pyro-DART-MS. It measures the effectiveness of heat destruction to remove PFAS-containing waste, for which a good resolution MS is mandatory, as the process is complex.

Aduluteration with coccidostat

von Holst et al. (2022) developed a DART-MS method to rapidly detect the presence of coccidiostats as the primary substance in feed additives. The study shows the benefit of DART-MS in detecting the unauthorized use of coccidiostats in animal feed without the need for any sample preparation, allowing a quick scan of the sample. The method allows for direct, fast screening without extensive sample preparation, enabling quick detection of these veterinary drugs in animal feed. The study highlights the potential of DART-MS for regulatory monitoring and quality control in the feed industry, ensuring compliance with safety standards and preventing unauthorised use of coccidiostats.

Mycotoxin detection

Tsagkaris et al. (2022) performed mycotoxin detection in cereal matrices using DART-Orbitrap MS and LC-MS and critically compared both methods. DART-Orbitrap MS enables rapid, direct analysis without the need for extensive sample preparation, while LC-MS offers higher sensitivity and specificity. The study evaluates the effectiveness of these methods in identifying and quantifying mycotoxins, highlighting the advantages and limitations of each approach. The findings support DART-Orbitrap MS as a valuable screening tool but emphasise LC-MS for confirmatory analysis in food safety applications.

DON analysis

Geballa-Koukoula et al. (2021) developed and validated a DART MS process for the analysis of Deoxynivalenol (DON) following initial screening with a smartphone-based lateral flow immunoassay. The method enables rapid and efficient DON analysis in food and agricultural samples, improving traditional detection workflows. The study validates the approach, demonstrating its sensitivity, accuracy, and applicability for real-world contamination assessment.

Esters and aflatoxins

Chen et al. (2022) developed a green analytical methodology with dispersive liquid-liquid microextraction-DART-HRMS for esters and aflatoxins. In an attempt to practice green analytical methodology with dispersive liquid-liquid microextraction-DART-HRMS analytical chemistry, where the physicochemical properties of the natural deep eutectic solvents (NADESs) were used for the extraction of esters and aflatoxins. For sample pretreatment, dispersive liquid-liquid microextraction (DLLME) was used. The solidified NADES extracts were melted and vaporised at elevated temperatures and analysed by DART-Q-Orbitrap HRMS for further spectrometry.

Seed toxins

Sisco et al. (2022c) used DART-MS for the fast screening of seed-based toxins. Without any sample preparation, seed toxins can be monitored. It can categorise toxins, set detection limits, and provide high-throughput screening for hazardous seed toxins, with applications in forensic, food safety, and regulatory fields.

Toxic compounds in PPE

Xu et al. (2025) developed an analytical method for PPE analysis using DART-MS. DART-HRMS,

combined with ATR-FTIR, enables the identification of additives and residual chemicals that can be toxic or hazardous, all without requiring pretreatment. Emphasising DART-MS's reliability in safeguarding health and safety can reassure the audience of its effectiveness in detecting hazardous substances.

Drugs-cathinones

Li et al. (2024) developed an automatic magnetic dispersive solid-phase extraction (MDSPE) combined with DART–HRMS for the analysis of synthetic cathinones. It is an ultrafast method for the quantification of 21 synthetic cathinones from urine samples using MDSPE followed by DART-HRMS.

4. Sample authenticity

Authentication of red wine

Lin et al. (2023) performed the rapid authentication of red wine using DART-MS with MALDI-MS. Efficient authentication of red wine is achieved through the rapid process of DART-MS with MALDI-MS. This study investigates the rapid authentication of red wine using a combination of MALDI-MS and DART MS, where the former technique provides molecular fingerprinting and the latter enables the fast, direct analysis of both volatile and non-volatile compounds. The combined approach enhances the identification of wine authenticity, detecting adulteration and variations in composition. This method offers a fast, reliable, and non-destructive tool for quality control and authentication in the wine industry.

QC testing of cocoa products

Rýdlová et al. (2020) developed a DART/TOFMS method for the QC testing of cocoa products in terms of authenticity and quality. This study examines the application of DART/TOFMS in assessing the quality and authenticity of cocoa products. The method enables rapid, non-destructive screening to differentiate between authentic and adulterated cocoa samples based on their chemical profiles. DART/TOFMS is an effective strategy for the QC analysis of cocoa products and rejection of adulterated products using characteristic markers. The origin of cocoa products can be verified based on the chemical profile, and it serves as a rapid and non-destructive QC method for cocoa products.

Saffron authenticity

De Angelis et al. (2021) developed a DART-HRMS method for the potential chemical markers identification to assess saffron authenticity. The utility of DART-HRMS to identify the potential chemical markers can be used to differentiate genuine saffron from tainted samples by focusing on the prime metabolites of genuine saffron. The results highlight DART-HRMS as a rapid and reliable tool for saffron authentication, offering a promising approach for food fraud detection and quality control in the spice industry.

History of poultry production

Birse et al. (2021) investigated the rapid evaporative ionization mass spectrometry vs DART-MS to analyze the history of poultry production. Two ambient ionization methods, based on Rapid Evaporative Ionisation and DART, can be used to gain insight into the production history of poultry. Based on the chemical profile of poultry meat, it is possible to differentiate between conventional, free-range, and organic farming systems for chicken production. Hence, ambient MS can be used for the QC analysis of poultry meat.

5. Drugs

Drug residues in bovine tissue

Khaled et al. (2020) devised a method based on SPME-DART-MS/MS for the detection of multiple drug residues in bovine tissue by a fast and high-throughput process This study demonstrates the effective use of SPME-DART-MS/MS for the high-throughput screening of bovine tissue for the presence of multi-residue pharmaceutical drugs. The approach minimises sample preparation while enabling fast, sensitive, and reliable detection of drug residues. The method enhances food safety monitoring by providing an efficient tool for identifying pharmaceutical contaminants in meat, supporting regulatory compliance and ensuring consumer protection against harmful drug residues in animal-derived products.

β-adrenergic agonist drugs

Shelver et al. (2021) used DART-MS for the screening of β-adrenergic agonist drugs in animal urine. The authors devised a DART-MS method to analyse β-adrenergic agonist residues in animal urine, which does not require tedious sample preparation or separation, drastically reducing the time.

Analysis of acid salts

Cody (2021) used DART-MS for the screening and qualitative analysis of acid salts. Organic acid salts are poor candidates for DART-MS due to their reduced volatility, and the problem can be resolved by adding a strong acid that can convert the salt to free acid. and further analyzed by DART-MS.

Detection of diazepam in plasma

Liu et al. (2021) applied a DART-MS/MS method for the pharmacokinetic study of diazepam. This study investigates the application of DART-MS/MS for the high-throughput and trace-level detection of diazepam in plasma. The method enables rapid analysis with minimal sample preparation, making it suitable for pharmacokinetic studies. Sensitivity and accuracy were assessed, demonstrating its potential for real-time drug monitoring. The study highlights DART-MS/MS as a better alternative to analysing benzodiazepines, offering a fast and efficient approach for clinical and forensic applications.

6. Miscellaneous

Paint

Laetsch III et al. (2025) evaluated the capabilities of DART-MS compared to FTIR spectroscopy and SEM-EDS for analysing architectural paint mixtures. DART-MS offers rapid, direct chemical profiling of organic components with minimal sample preparation, demonstrating its practical value. Highlighting its speed and simplicity can help the audience feel confident in its usefulness for forensic, conservation, and materials science applications.

NOC

Batista Junior et al. (2024) developed a DART-MS method for the detection and quantification of N-nitrosamines in Drugs. The method can be applied to pharmaceuticals, in solution form or as tablets, as a preferred approach due to its high-throughput analysis, minimal sample preparation, and simplicity.

TATP release from canine training devices

Simon et al. (2021) established the use of DART-MS to detect the released triacetone triperoxide (TATP) from polydimethylsiloxane (PDMS)-based kennel training aids. Canine training aids use TATP-based devices, and the volatile substances can be easily monitored using DART-MS in real time. The research demonstrates that PDMS-based aids release lower yet detectable levels of TATP vapour, making them effective for canine training. The study highlights the importance of volatile release characteristics in training aid development and suggests DART-MS as a reliable tool for monitoring explosive vapour emissions in real time.

Drawbacks

Although DART-MS has many benefits, for trace elements, the analyte content must be enriched before analysis. To achieve better results, three options are typically employed, namely dilution, purification, and derivatisation. DART-MS shows discrimination in terms of the states of matter. A close analysis of the DART-MS research data reveals that more liquid samples are studied compared to solid samples. Liquids have a lower level of detection, which may be due to the faster ionisation and evaporation that amplify the sample concentration in liquid samples compared to solid samples, where a small proportion of the sample reaches the MS, leaving the majority aside, as DART is a surface phenomenon. Therefore, when comparing the DART-MS results, it is essential to consider whether the matter is in a solid or liquid state (Dong, 2017). Another significant disadvantage arises due to complex samples with overlapping spectral lines, as the technology lacks chromatographic separation.

Another issue is with compounds having labile bonds, as in glucuronides, which rupture upon ionisation. It is also problematic when the analyte's mass exceeds 1000 Da. There is a need for other ionising gases apart from He and Nitrogen. Helium is more widely used and its cost needs to be considered. Instrument's size reduction is another area that attracts the portability of the device for applications such as forensic samples, where a fast response is crucial in criminology.

CONCLUSION

DART-MS is a remarkably versatile ionisation technique that has revolutionised the scope and applications of mass spectroscopy. It finds use in a multitude of fields, from drugs in dosage forms or biological fluids, to forensic science, pesticides in fruits, vegetables, or animal tissues, categorisation of microorganisms based on lethality, and timber grading. DART-MS, an ambient ionisation technique, has several uses in forensics, food adulteration, atmospheric pollution monitoring, drug detection, etc. This technology's adaptability to the sample state is what makes it so fascinating. It makes it possible to sample solid, liquid, or gaseous phases without the need for sample preparation or pretreatment. Any size or shape of material, regardless of its state, can be ionised under ambient circumstances in the open air thanks to this unique ionisation process. As an ambient ionisation strategy, DART-MS offers wide application for food adulteration, forensics, pollutant monitoring in the atmosphere, presence of narcotics, etc. What makes this technology truly intriguing is its flexibility with respect to the sample state. It enables the sampling of solid, liquid, or gaseous states without any sample pretreatment or preparation. This new ionisation technique allows the ionisation of any-sized or shaped material, regardless of its state, under ambient conditions in open air. It allows for quick mass spectroscopy examination for both quantitative and qualitative applications when paired with a TOF or other better mass analyser. Its quickness and low sample preparation requirements are its most noteworthy characteristics. Without the need for chromatographic separation or sample preparation, it enables the ionisation of low-molecular-weight species on the surface of solid or liquid samples. This greatly shortens the time required for each sample, enabling high-throughput screening and lowering analytical costs. This method's adaptability is demonstrated by the large amount of research that has been done with it, as evidenced by the published literature. Analysing any subject can yield both quantitative and qualitative findings. DART-MS technology can quickly prepare each organ's chemical fingerprint and integrate it with machine learning. This makes it easier to identify illnesses early and can have a big impact on the medical industry. With this technology, databases that may be utilised to develop certain algorithms that, when paired with machine learning, allow for the quicker categorisation of objects based on authenticity can be created after analysing various members of a group.

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AUTHOR CONTRIBUTION STATEMENT

The review manuscript was written with the contributions of all authors. All authors have read and approved the final version of the manuscript.

CRediT: (CM) conceptualization, investigation, data curation, formal analysis, validation, writing-original draft, writing-review & editing, (JB) conceptualization, investigation, methodology, validation, writing-review & editing, (SM) conceptualization, investigation, formal analysis, resources, supervision, writing-review & editing, (ADP) conceptualization, methodology, validation, writing-review & editing, (KB) conceptualization, methodology, validation, writing-review & editing.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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