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Portable Mass Spectrometer: Mini Review

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Abstract Mass Spectrometry has now turned into a giant subject in itself, with its varied features and uninterrupted technological enhancements it has become so huge that various types of Spectrometers are studied separately. This paper covers the objectives, importance, designs, configurations and wide applicability of field portable mass spectrometer. The study further dictates how the varying configurations suit vivid real life problems and how Portable Mass Spectrometer has come to rescue to such problems.

Keywords — Compact Mass Spectrometer, DESI, DART, ESI, Forensic Science MS, Warfare agents MS

I. INTRODUCTION TO MASS SPECTROSCOPY AND SPECTROMETER

Mass spectrometry is an analytical technique that measures the composition and quantity of species in the particular sample. The principle behind mass spectroscopy is that it first ionizes chemical species via different methods (e.g. bombarding it with electrons) and then sorts the ions based on their mass-to-charge ratio, this is done by accelerating them in presence of external force field (may be electrical or magnetic) and this deflects ions of same mass to charge by same angles. These deflected ions are captured by a special mechanism (e.g. electron multiplier) and the identification is shown as spectra of the relative abundance of detected ions as a function of the mass-to-charge ratio.

The common desired features of a Mass Spectrometer are as follows: [1]

(a). Mass Range: It is desired to have highest possible mass to charge ratio amenable to analysis. A higher value will always be useful for samples having high mass compounds.

(b). Resolution: It is the measure of ability to separate two neighbouring mass ions. Higher resolution betters the results for separating isotopes and isotones.

(c). Efficiency: It is the amount of ions formed per cycle of ionization. Higher the efficiency lower will be the time required for sample testing and also amount of sample required will be less.

(d). Mass Accuracy: It is defined as the measured value of mass to charge ratio in comparison to actual (accurate) value of mass to charge ratio. Higher the mass accuracy better is the spectrometer.

(e). Linear Dynamic Range: The range over which an ion signal is straight with the analyte signal.

(f). Speed: It is measured as number of spectra captured per unit time.

A quick scan is required for swiftly altering events. A slow speed is considered necessary in true mass measurement experiments.

(g). Sensitivity: It is expressed in terms of abundance or detection sensitivity.

(h). Adaptability: The eligibility of spectrometer for outfitting several ionization techniques and other ancillary devices, so as to work for wide variety of samples.

(i). Other important characteristics include simple design; construction and control, less power consumption, high operational reliability, economical and small size (in terms of dimensions as well as mass), though mentioned at last but in the contemporary are in great demand and has zeal for research.

The need for low cost and compact spectrometer is essential because one cannot afford expenses more on analytical techniques then the actual research itself besides being compact and handy helps people to implant it in other machines or equipments or objects as well as to carry it at distant places to get on time analysis instead of making efforts to bring samples back to one place.

Current edge technologies in the ideation, design, amalgamation and optimization of small, portable analytical mass spectrometers (MS) and ion mobility spectrometers (IMS) has allowed development of ‘field laboratories’ for a wide range of application areas including environment sciences, medical sciences, defence and security, quality

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assurance, space exploration, etc. This has provided an advantage in information assisting and augments the process of useful decision-making at the point of analysis (PoA). Several advantages of mini mass spectrometers include;

(a). Chemical investigation in harsh environments,
(b). Great sensitivity,
(c). Detects even very low limits,
(d). Rapid response times
(e). Variety of mixtures can be tested (organic, inorganic, volatile, non-volatile, etc.).
(f). These also allow characterization of small, large, single analyte and complicated analyte mixtures. [2]

Figure 1: Model: Innov X Omega XRF Handheld Xray MS

II. DESIGN AND CONCEPT OF PORTABLE MASS SPECTROMETER

Chen et al proposed three different designs of sampling probes for small mass spectrometers. They used the technique of ambient ionization along with sampling probes. In the first concept, they used a long SS tube for conveying the desorbed ions using DESI (desorption electrospray ionization) from the ambient ionization source destined to vacuum manifold. For medical purposes it is suggested to use rapid evaporative ionization mass spectrometry system (REIMS) such that tissues are ionized using a doctor's knife and the sample is henceforth sent to MS. In the next approach, the sampling or the ionization zone was kept near to the vacuum manifold whereas an extending connection was made between manifold and vacuum pump. The vacuum pump is integrated with backing pump and the control system. The ion introduction was conducted using discontinuous atmospheric pressure interface (DAPI). In the last concept, the vacuum pump was joined with compact sampling unit whereas the long line was planted between sampling unit and backing pump/control electronics package. [3]

Kogan et al also suggested designs for portable MS in terms of dynamic and static models They suggested that for laboratory purposes static models are useful because of their simple design construction and control, better sensitivity and feasibility of measuring different parts of spectrum. To have studies dealing with space research, geophysical research, environmental check, medical diagnosis and process control it is advantageous to have dynamic models with time-of-flight systems for dealing with parallel mass and energy balance. The authors have suggested design of static portable MS using ion optic design with separate electric and magnetic fields for ionization and spectra detection. This ion optic analyzer is integrated with Nier type ion source, an electrostatic and a magnetic field and two assisting electron multiplier detectors. The next part is injector, gas inlet flow is controlled using by piezoelectric injector voltages and is brought to steady state using automatic valve for gas flow. The extremely high vacuum is attained using sputter-ion pump and lastly the electronic controls and softwares. [4]

Gard and his co-workers designed a portable MS for detecting aerosols using time-of-flight technique refereed as ATOFMS (Aerosol Time-of-Flight Mass Spectrometer). These MS are compatible in analyzing both positive ions and negative ions obtained post-ionization of aerosols and can be travelled to any place and work while in motion. These have been proved as boon for studying of production, structure and effects of aerosols in atmospheres. [5]

Polycyclic aromatic hydrocarbons (PAHs) and alkyl substituted benzenes are noxious, carcinogenic and mutagenic in nature, and thus their presence in environment produces harmful effect on life forms. It thus becomes essential to identify their presence in the environment. Use of swift, efficient, portable MS with Desorption atmospheric pressure chemical ionization (DAPCI) has been proved to be an excellent analyzer. Stephan Taylor and his co-workers have used the same to characterize: [6]

- 1,2,3,5-tetramethylbenzene,
- fluoranthene,
- anthracene,
- benzo[k]fluoranthene,
- pentamethylbenzene,
- hexamethylbenzene,
- acenaphthene,
- dibenz[a,h]anthracene,
- indeno[1,2,3-c,d]pyrene,
- 1-benzyl-3-methyl-naphthalen,
- 9-ethylfluorene

One of the advances in the portable mass spectrometer is application of Ambient Ionization technique. In this process, ions are generated outside the confinement of Mass Spectrometer. Here, two different phenomena takes place, namely introduction and ionization and both of them can be controlled individually. The ambient ionization technique is advantageous in terms of shorter analysis time, high vacuum

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is not required and can be applied to large variety of specimen. Moreover, the ambient ionization techniques do not contaminant the sample. The most common types of abient ionization techniques include:

a) Desorption Electrospray Ionisation Mass Spectrometry (DESI-MS): Here a solvent spray of charged molecules is directed towards the surface of interest.

b) Direct Analysis In Realtime (DART): In this method the ionized molecules are desorbed from a surface by any inert gas glow discharge of excited-state atoms produced by an electric field.

c) Plasma Assisted Desorption Ionisation (PADI): Here, instead of inert gas glow discharge a cool plasma source is used for ionization and desorption.

d) Extractive Electrospray Surface Ionisation (EESI): It works with gentle sampling process that uses two separate sprayers. A gas is allowed to flow over the specimen of interest to desorb the molecules and the gas is then directly inserted into the electrospray region of ESI-MS to ionise the molecules.

e) Desorption Atmospheric Pressure Chemical Ionisation (DAPCI): Here, analytes are desorbed and ionised using gas-phase projectile ions created by an atmospheric pressure corona discharge in the vapour of solvents. [7]

III. APPLICATIONS

A. Aerospace Technology

The primary objectives of Mass Spectrometer in space technology are: [8]

(A) Gas analysis in atmospheres of various celestial bodies; Venus (1972 – 1978), Mars (1970 – 1978), Jupiter and Galileo (1989 – 1995), Saturn and Cassini (1997 – 2004), other comets and bodies (2002 – 2018 (alongside with modern technology blend)).

The Atmospheric gas analysis is of interest for many reasons. To quote a few: The precise constituents and compositions of the atmospheres give the history of evolution of planets and the solar system. Second, identification of organic substance in the lithosphere will sprout the suggestion of either existence or possibility of sustenance of life on the heavenly body. Third, the potential compounds may it either be gases or acids or alkalis may or may not be similar to those present on earth and amidst differences can be far too wide to guess.

The use of Remote sensing based spectroscopes in place of MS has always been a lucrative approach but the former restricts itself to the higher magnitudes of concentration range whereas later can be used for up to 8^{th} power of concentrations. (It is important to understand that such missions depend on way possible precisions). More practically, the two are used in parallel to each other for better insights.

(B) Monitoring VOCs in cabin air samples from manned space missions.

In manned space vehicles maintaining the cabin atmosphere is one of the crucial aspects, unlike the earth's atmosphere there is no availability of life sustaining environment in outer space and thus, to support the astronomers it becomes necessary to create and maintain artificial atmosphere, popularly known as Environmental Control and Life Support System (ECLSS). There are several possibilities of contamination of this atmosphere, for example, human metabolites, out-gassing from materials and thermal degradation by-products.

The minute and precise analysis of this artificial atmosphere so created inside the shuttle is easily monitored using Portable and Light Mass Spectrometer. Other important applications of Mass Spectrometer in Space are as follows:

- Investigation of breathing to study the consequence of microgravity on respiratory system.
- Identification of propellant leaks prior to launches of the Space Shuttle
- Identifying the sources of coolant or fuel leaks external to spacecraft during extravehicular activity.
- Validating the performance of trace contaminant removal in advanced life support systems.

Well, despite being so advantageous some limitations are possessed by Mass Spectrometers, viz.:

- In the analysis mixture containing fragment and doubly charged ions using MS per mass resolution can set hurdles in the data interpretation.
- The inlet of analyzer may get adulterated if comes in contact with fuel emissions or noxious waste from off-gassing of materials from the spacecraft.

B. Analysis of Chemical Warfare Agents

Chemical Warfare Agents are substances that are intended for military purposes to be lethal, seriously injure, or incapacitate target individuals because of their physiological effects. Mass Spectrometer along with Gas Chromatographer (GC-MS) has mixed capabilities of various equipments. It has high sensitivity of an ion mobility based systems (IMS), the dynamic range of a photoionization detectors (PIDs) with and without a GC or a flame ionization detector (FID), the specificity of a gas detection system, tube system, or card kit, and adds the selectivity required for rapid identification of many organic compounds. [9] Contreras *et al.* successfully used Hand-Portable Gas Chromatograph-Toroidal Ion Trap Mass Spectrometer (GC-TMS) to identify Chemical Warfare agents such as nerve agents sarin (GB), soman (GD), cyclosarin (GF), VX and blister agent mustard (HD) using 50 µg/mL each in isopropanol. [10] Smith *et al.* used hand-portable gas chromatograph–toroidal ion trap mass spectrometer for auto chemical ionization for four of degradation products related to O-ethyl S-(2-diisopropylaminoethyl) methyl phosphonothiolate (VX). In his experiments he used a gas chromatographic inlet with electron ionization. The protonation of analytes was seen for all conditions except for the largest analyte, bis(diisopropylaminoethyl)disulfide which yielded $[M+H]^+$ ions only with increased fixed ionization or ion cooling

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times. [11] In fact, the US Army worked on a project couple of decades back were in, they planned to characterize and destroy non-explosive and distributed chemical weapons. In order to do show they designed and constructed mobile munitions management device (MMD) containing analytical test equipment and engineered in such a way that personnel safety and munitions destruction effectiveness was at the best. Many experiments were performed to establish the usefulness of the device in measuring known CWAs and industrial gases generated from various locations within the trailer. The GC-MS operated in selected ion monitoring and gave real time data of remotely located munitions treatment vessel (MTV). [12] Yang *et al.* proposes the use of Palm Portable Mass Spectrometer (PPMS) for a step ahead in military applications towards biological warfare -agents by identifying the fatty acids presents in the pyrolized living organism; although there isn't any current literature citing the successful use of MS in detection of Biological Warfare Chemicals. [13]

Smith *et al.* identified mixtures containing 4 chemicals diethyl malonate (DEM), methyl salicylate (MeS), dimethyl methylphosphonate (DMMP) and 2- chloroethyl ethyl sulfide (CEES). They used glow discharge electron ionization (GDEI) at the source and mass was analyzed using cylindrical ion trap (CIT). [14]

C. Forensic Sciences

Morelato has discussed and assessed the several literature which has used Portable Mass Spectrometer in integrated with DESI for analysis of drugs of abuse in urine and plasma specimens, finger print analysis, inks and documents, explosives and chemical warfare agents. The study suggests that use of DESI-MS is profitable in terms of minimum sample required, sensitivity of detection, ease of transverse and negligible sample deterioration. [7] Eckenrode has mentioned the application of GC-MS in Forensic studies and has shown how the advances have proved to be a boon towards evidence identification even in harsh situations like forest. [9] A small size mass spectrometer which can be easily mobile can be used as chemical analyzer in real-time in the field, such as air contamination monitoring and odor investigation on the crime scenes, the detection of illegal trafficking of drugs and explosives for homeland security. [13] In fingerprint analysis, use of DESI based MS has provide great results in identifying, if any explosives or substance of abuse has come in contact of suspect or victim. These results provide an insight regarding the motive or motion of crime. Using a portable form of MS will help conduct the tests at the crime scene without any contamination of sample collected. [15]

Keil *et al* [16] developed a miniature hand-held mass spectrometer by adjoining atmospheric pressure ionization methods, electrospray ionization (ESI) and desorption electrospray ionization (DESI). It consists of a rectilinear ion trap (RIT) mass analyzer and is operated on battery. It is small to be carried in hand but strong to handle various environments. (total system: 10kg, 0.014m^3 and 75W power consumption). It has an atmospheric inlet, consisting of SS capillary tube was used to introduce gas into the vacuum chamber. The instrument is used at 15mTorr. ESI and DESI sources were used to generate ions. The instrument was used for testing of:

(a). Aqueous mixture of drugs

(b). Analysis of peptides

(c). Cocaine samples present on different surfaces like currency notes

There tests showed the following conclusions:

(a). Atmospheric pressure ionization is possible for simple portable MS systems

(b). Detection limit can be as low as parts per billion.

(c). Successful application even in high pressures

(d). Can be used for completely different sets of mixtures

Successful attempt of coupling ESI and DESI in portable MS.

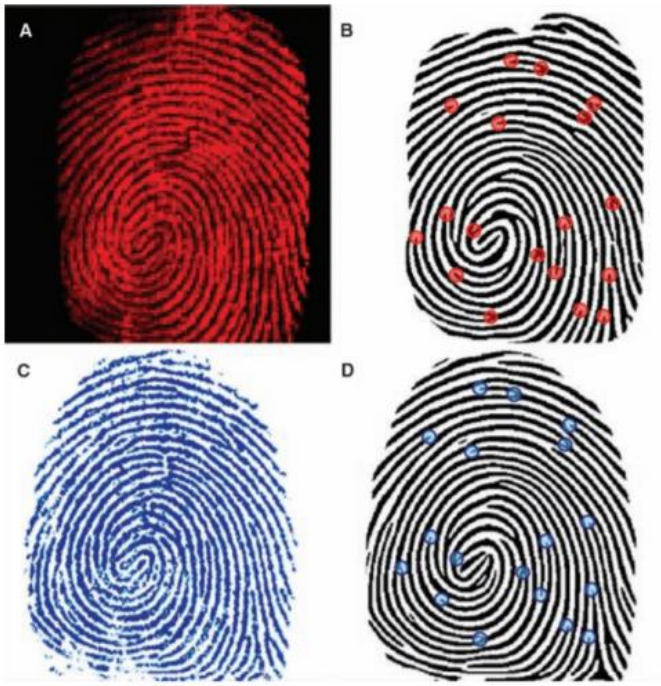

Figure 2: (A) DESI image distribution of cocaine on a Latent Finger Print. (B) Computer generated fingerprint from DESI image. (C) Ink fingerprint optically scanned. (D) computer-generated fingerprint from optical image.

Source: www.sciencemag.org/cgi/content/full/321/5890/805/DC1

D. Waste Water Treatment

Contreras *et al.* [10] showed that GC – TMS can be successfully used for tetrachloroethene and bromoform. A standard mixture of the EPA Method 624 volatile halocarbon compounds was diluted to 20 ppm in water, and SPME sampling was performed as previously described. Separation of the mixture was achieved in <65 s. This separation showed the ability of the portable GC-TMS system to rapidly separate and identify organic compounds in complex mixtures. The peaks of the spectra clearly identified compounds such as:

- 1,1-dichloroethane,
- methylene chloride,

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- trans-1,2-dichloroethene,
- 1,1-dichloroethane,
- chloroform,
- 1,2-dichloroethane,
- 1,1,1-trichloroethene,
- benzene,
- carbon tetrachloride,
- 1,2-dichloropropane,
- trichloroethylene,
- bromo-dichloromethane,
- 2-chloroethyl vinyl ether,
- cis-1,3-dichloropropene,
- trans-1,3-dichloropropene,
- toluene,
- 1,1,2-trichloroethene,
- di-bromochloromethane,
- tetrachloroethene,
- chlorobenzene,
- ethyl benzene,
- bromoform,
- 1,1,2,2-tetrachloroethane,
- 1,3-dichlorobenzene,
- 1,4-dichlorobenzene,
- 1,2-dichlorobenzene.

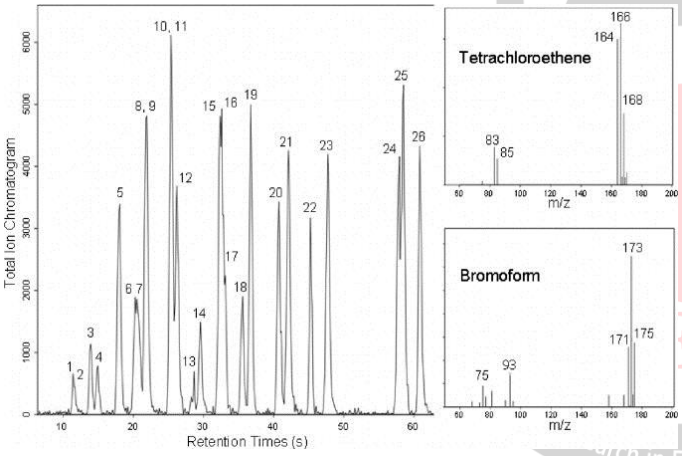

Figure 3: Spectra showing peaks amongst complex substance mixtures.

Source:
https://www.sciencedirect.com/science/article/pii/S1044030508005655
[16]

E. For Oil Leakage and Adulteration Detection

Electrospray ionization mass spectrometry (ESI-MS) is directly infused into aqueous methanolic extracts of biodiesel samples for simple, quick and reliable testing in terms of: [17]

a) identification of alcohol used for ester production

b) monitoring degradation of biodiesel

c) counting adulteration rates

d) measuring quantities of left over glycerine and glycerides

The portable MS with the help of 473 nm laser-induced fluorescence (LIF) and multi variate analyzer is also been used to study the adultration of virgin olive oil which contains extra-ordinary quantities of antioxidants and monounsaturated fatty acids. The same study has also been carried out with Rapeseed, Peanut and Mixed Oils. [18] On the similar lines easy ambient sonic-spray ionization mass spectrometry (EASI-MS) has also been used to analyze oils. The technique is used for on spot qualitative measurement of TAG (triglycerides) in the oil. [19]

F. Environment Monitoring

The in-situ measurement of volatile pollutants and metabolic gases is desired in order to gain real time information along with minimization of disturbance and discarding the need of sample collection and transportation. One of the oldest designs of Portable MS was developed on the concept of compact cross-field analyzer with the aid of high energy product magnet and control circuitry working under minimum power source of around 12V. [20] Though this is sort of obsolete but researchers globally have now been successful in use of MS for environment analysis.

Researchers from University of North Carolina have provided a critical review on the use of Mass Spectrometers for monitoring tropospheric aerosols. The authors clearly cite that attempts have been made by various researches globally for use of different types of Aerosol Mass Spectrometer. NOAA's particle analysis by laser mass spectrometer (PALMS), University of California at Riverside's Aerosol Time-of-Flight Mass Spectrometer (ATOFMS), University of Delaware's Rapid Single-Particle Mass Spectrometer (RSMS) and Aerodyne's Aerosol Mass Spectrometer (AMS). In terms of environment monitoring following parameters are measured: wind direction and velocity, pollutant levels (ozone, CO, CO_2, NOx, etc.), relative humidity, and particulate matter. [21] One of the common environmental uses of MS is in identification of gases released from the industries. Use of compact MS has benefited both the industrialists in terms of installing MS directly at the apex of chimney as well as the environment auditors in terms of handling MS in hand while analysing chimney off-gases.

Gao *et al.* successfully studied the experiments of identifying toluene vapor in air and for an aqueous naphthalene solution using membrane sample introduction via a small rectilinear ion trap mass analyzer rectilinear ion trap mass analyzer. [22], [23] Lebedev in his study has mentioned the utmost importance of Mass Spectrometer in environment contaminant characterization. He is characterized Mass analyzers under 4 categories: Gas Chromatography – Mass Spectrometer (GC/MS), Liquid Chromatography – Mass Spectrometer (LC/MS), High-resolution Mass Spectrometer (HRMS) and tandem Mass Spectrometer (MS/MS). The review studies the use of these MS for contaminant grouped in categories of Pharmaceutical Waste, Personal Care Production Waste, Flame retardants, Perfluorinated Compounds, Disinfection By-Products and others including detergent and surfactant industry, Selenium Compounds and Nitroaromatic compounds. Though the paper suggest use of MS for almost all variety of wastes; there aren't enough study of waste from organometallic compounds. He suggests that researchers are bending towards identification of target

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analytes and a current interest has developed in non-target analytes too. [24]

IV. CONCLUSION

The current study clearly shows how field portable mass spectrometer turns out to be modern angel in terms of chemical analysis in several fields and it possess all the desired characteristics of a reasonable mass analyzer, viz., speed, portability sensibility, precision, simple construction and cost efficient. Though, it lacks in some terms, such as, there is no one single type of portable mass spectrometer which can be used to all domains, one has to trade off between lightness and ionization speed, and so on. However, in over all terms a field portable mass spectrometer is a great boon in the field of Chemical Analysis.

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