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## A review of the development and application of space miniature mass spectrometers

Zhengyi Ren, Meiru Guo<sup>\*</sup>, Yongjun Cheng, Yongjun Wang, Wenjun Sun, Huzhong Zhang, Meng Dong, Gang Li

Science and Technology on Vacuum Technology and Physics Laboratory, Lanzhou Institute of Physics, Lanzhou 730000, China

### ARTICLE INFO

#### Keywords:

Miniature mass spectrometers  
Space application

### ABSTRACT

This article reviews the recent development and application of four types of space miniature mass spectrometers including magnetic sector mass spectrometer, quadrupole mass spectrometer, ion trap mass spectrometer and time-of-flight mass spectrometer. The advantages and the disadvantages of such mass spectrometers are briefly discussed. Finally, the expectations for improved properties and development trends of these mass spectrometers are presented.

### 1. Introduction

With the development of space science and technology, space exploration and manned space missions have become increasingly frequent [1–3]. The scientific objectives of these tasks are mainly focused on exploring biological and life matters, the origin of life and the evolution history of the planets, as well as searching for the planet's resources and space for human survival [4,5]. The realization of these objectives is closely related to the determination of their chemical composition, for which the commonly used methods include colorimetric tube, electrochemical sensor, pressure measurement, spectrometry and mass spectrometry. As a matter of fact, the colorimetric, pressure measurement and electrochemical sensor methods are usually used to monitor specific gases. For example, the colorimetric tube is used to monitor the CO<sub>2</sub> gas concentration at the space station [6,7]. Spectrometry is based on different chemical structure of the gas molecules which differ in wavelengths of light absorption or the excitation itself to obtain a specific spectrum for analysis. It has also been applied in space, such as the Spectroscopy for Investigation of Characteristics of the Atmosphere (SPICA) for Mars flown on Mars Express satellite launched in 2003 [8,9], SPICA for Venus aboard Venus Express in 2005 [10]. Mass spectrometer (MS) analyses gas components by separating ions of different mass-to-charge ratios. It can obtain information on the composition, atomic or molecular weight, molecular structure, and molecular arrangement in the material. This information is difficult to obtain by other avenues. For example, NASA only detected the H and O atoms on Mars in 2004 using the Mini-TESS spectrometer which inferred the existence of water [11,12]. Until Phoenix equipped with a magnetic

sector MS launched in 2007, the first direct detection of water on Mars has provided indication for potential existence of living matter [13]. Therefore, compared with other instruments, the MS provides more detailed information of the measured, and plays an irreplaceable role in identifying gas components in space exploration.

Since the first MS developed by Thomson [14,15], space miniature mass spectrometers are widely used for various scientific objectives due to their high sensitivity, good selectivity, high precision, and high resolution power [16–19]. Mass spectrometers can be divided into magnetic sector MS, quadrupole mass spectrometer (QMS), ion trap MS, and time-of-flight (TOF) MS according to their operating principles. The four types of mass spectrometers cover detection tasks range from the Earth's orbit to deep-space environment, and outer planet surfaces. The detection targets include the atmosphere of the planet, solar wind, dust particles, planet soil, and rock composition. At the initial stage of space exploration, mass spectrometers were mainly used to observe the ionospheric atmosphere densities, neutral gas composition and positive ions, including detection of O<sub>2</sub>, N<sub>2</sub>, noble gases, H<sub>2</sub>O, CO, CO<sub>2</sub>, NO, and NO<sub>2</sub> [20–22]. Later on, with the continuous development of aerospace technologies, human beings were finding more and more energy and living space of outside the earth. For example, the magnetic sector MS has found <sup>3</sup>He in the lunar atmosphere, and there may also be molecular hydrogen [23]. Small organic molecules were detected on Venus [24]. In addition, the QMS carried by Cassini on Saturn, flown on Galileo detected possibly PH<sub>3</sub> and Cl on Jupiter.

In detail, this article reviews the application of four types mass spectrometers in space, including the main parameters of mass spectrometers, such as volume, power consumption, mass range, and

<sup>\*</sup> Corresponding author.

E-mail address: [meiruguo510@163.com](mailto:meiruguo510@163.com) (M. Guo).

resolution for each mission. The goal is to guide the design and development of mass spectrometers for excellent scientific data return in future space exploration missions.

## 2. Magnetic sector MS

The principle of magnetic sector is that ions enter into a constant magnetic field, and then according to the difference in mass-to-charge ratio to achieve ion separation. The ratio of mass-to-charge ( $m/q$ ) can be expressed by equation (1) [25], where  $B$  is the magnetic field,  $U$  is the ion accelerating voltage.

$$\frac{m}{q} = \frac{r^2 B^2}{2 U} \quad (1)$$

This shows if the radius  $r$  is imposed by the presence of a flight tube with a fixed radius  $r$ , for a given value of  $B$  only the ions with the corresponding value of  $m/q$  can go through the analyzer. Changing  $B$  as a function of time allows successive observations of ions with various values of  $m/q$ .

The magnetic sector MS has been loaded on many probes, and has completed the space exploration missions remarkably well. It has following advantages for space exploration: (1) simple design; (2) good stability; (3) solid structure; (4) high mass resolution capabilities; (5) superior abundance sensitivity. However, it is not suitable for measuring large mass of gas molecules or organics in fast analysis situations. Besides, miniaturization of magnetic sector MS leads to reduced performance because when the instrument gets smaller the uniform magnetic field is smaller, then the fringe magnetic field has a great influence on the properties of the MS. Miniaturization and performance are contradictory, which needs trade-off when designing the instrument. It is common to sacrifice the performance of the instrument to make the MS smaller, lighter, and consumes less power.

Most of the space applications of the instrument were focused on detecting the gas composition. Although there were many missions to observe the gas composition of the Earth's upper atmosphere and planet, the quantitative data were still incomplete. The first flight of the neutral gas MS occurred on June 6, 1963, an Aerobee rocket was successfully launched with two magnetic sector mass spectrometers [26]. One was a Nier-type double-focusing magnetic sector MS including an electrostatic analyzer in tandem with the magnetic analyzer, and the other was a 90° single-focusing magnetic sector MS (see in Fig. 1). The instrument mainly measured the neutral gas composition in the range of 100-km to 200-km. In addition, three single-focusing magnetic sector mass spectrometers employed to measure the number density of the upper atmosphere in the range from 120 km to 200 km [27]. However, the atmospheric densities frequently increase below 100 km and the MS can hardly work if there was no pump to maintain the pressure. In order to avoid the problem, Mauersberger [28,29] developed a Mattauch-Herzog (M – H) type double-focusing magnetic sector MS with a cryopump.

In addition to measuring atmospheric composition, magnetic sector mass spectrometers were also optimized for ionospheric compositions studies. For example, an Argo D-4 rocket was launched by NASA in January 17, 1964 employed the single-focusing magnetic sector MS [30]. The QMS flown on the Explorer XXXI satellite to measure the composition of the Earth's ionosphere as shown in Fig. 2 [31,32]. Besides, the Isis-2 satellite, in a nearly constant altitude (1400 km) orbit, carried a single-focusing magnetic sector MS that was launched in April 1, 1971 [33]. A few months after that, another flight of an Argo D-4 rocket, the positive ions composition was investigated using the single-focusing MS in the D- and E-layers and  $H^+$  become the dominant species above 420 km [34].

In the 1970s, Nier et al. [35,36] developed an open-source neutral MS flown aboard the Atmosphere Explorer (AE) -C, D, E satellites. The instrument is an M – H geometry double-focusing magnetic sector MS.

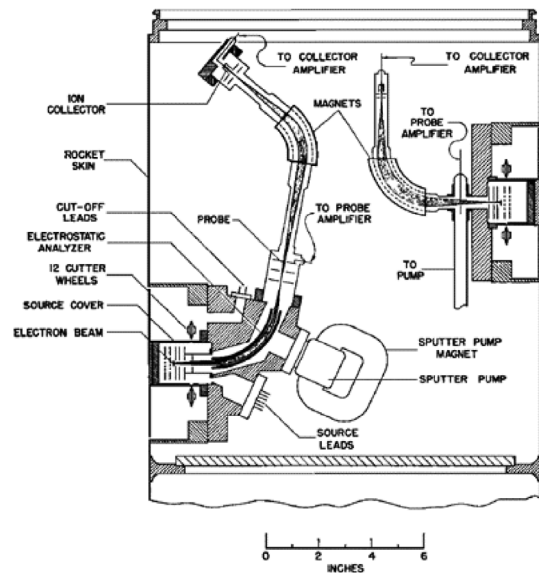


Fig. 1. Schematic view of cross section of rocket showing mounting of mass spectrometers. Reprinted with permission from Ref. [26]. Copyright 1964, J. Geophys. Res.

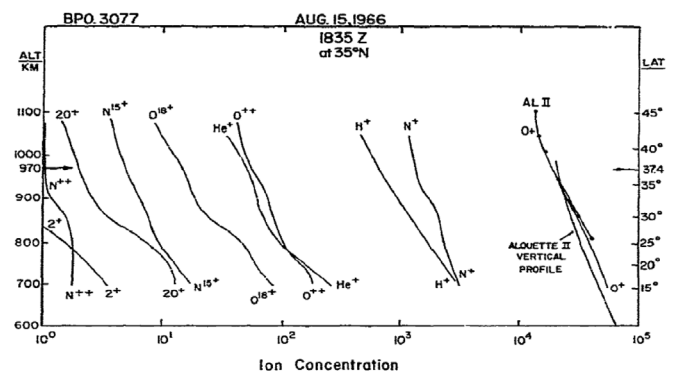


Fig. 2. Typical low altitude data showing ion concentration versus altitude and latitude. Reprinted with permission from Ref. [31]. Copyright 1969, Proc. IEEE 57.

The M – H type is selected because the instrument is compact and has relatively low power consumption. In addition, linearity to relatively high pressures is obtainable, and the geometry has a line of focus which allows a multiple-ion collector system to sample more than one mass number simultaneously [36]. The instrument structure is shown in Fig. 3. To study the low-to mid-latitude thermosphere during periods of low to moderate solar activity, Oppenheimer et al. [37] construct a model based on various ion densities by ion MS flow on AE-C satellite. In addition, the instruments on the Explorer XVII satellite [38] which developed by Hoffman et al. [39] are applied in space and completed a series of experiments.

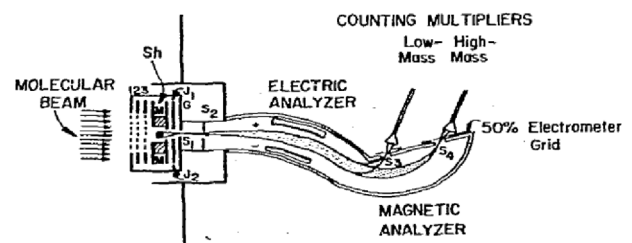


Fig. 3. Schematic drawing of the AE open-source spectrometer. Reprinted with permission from Ref. [35]. Copyright 1973, Radio Sci.



Fig. 4. Mass spectrometer on lunar surface. Reprinted with permission from Ref. [40]. Copyright Apollo 17 Preliminary Science Report.

Both Apollo 15 and 16 carried the single-focusing magnetic sector MS. Apollo 17, launched by the United States on December 6, 1972, also carried the single-focusing magnetic sector MS equipped with three mass channels whose mass ranges are 1–4 amu, 12–48 amu and 27–110 amu, respectively. Fig. 4 shows the instrument deployed on the lunar surface by the mission crew. The weight of the MS is 9.1 kg and the volume is 17 cm × 32 cm × 34 cm [40]. Apollo 17 mission has proved that the Lunar surface contains  $^3\text{He}$  and may be molecular hydrogen. The instrument measured Ne concentration was  $7\text{--}9 \times 10^4 \text{ cm}^{-3}$  in the nighttime. The sunrise to sunset ratio of  $^{40}\text{Ar}$  was 5, and their corresponding concentrations of  $3.5 \times 10^4 \text{ cm}^{-3}$  and  $7\text{--}8 \times 10^3 \text{ cm}^{-3}$ , respectively [41].

In the mid-1970s, the neutral MS on Viking I indicate that the upper atmosphere of Mars was composed mainly of  $\text{CO}_2$  with trace quantities of  $\text{N}_2$ , Ar, O,  $\text{O}_2$ , and CO [42]. The mass analyzer was a Nier-Johnson double focusing magnetic sector analyzer, the power consumption of the MS is 140 W with an approximate weight of 20 kg. In 1978, a Bus Neutral Gas Mass Spectrometer (BNMS) was designed to measure the number densities of neutral constituents in the Venus exosphere and thermosphere during its descent through the Venus upper atmosphere aboard the NASA Pioneer Venus multiprobe. The BNMS was a double-focusing magnetic sector MS [43]. It had three mass channels covering the range from 1 to 3, 4–8, and 12–46 amu, respectively. In addition, a single focusing magnetic sector MS was equipped on the “Pioneer Venus” that launched to detect atmosphere components below 62 km of Venus whose ionizer is electron impact (EI) source [24,44]. It has two mass ranges, one is 1–16 amu (low mass range) and the other is 15–208 amu (high mass range). The data of the MS revealed that compared with Earth, Venus has more Ar and contains 96%  $\text{CO}_2$ , 4%  $\text{N}_2$ . Ar isotopes, the  $^{36}\text{Ar}/^{40}\text{Ar}$  ratio possessing higher proportion than that of the Earth. The ratio of  $^{36}\text{Ar}/^{40}\text{Ar}$  was 85%, and the ratio of  $^{38}\text{Ar}/^{36}\text{Ar}$  was 20% [45]. The content of  $\text{O}_2$  was very low below 30 km. It was the first time confirmed that the dominant sulfur compound is COS.  $\text{SO}_2$  may exist below the clouds at a mixing ratio of the order of 100 ppm, while in the clouds it is less than 10 ppm [46].

For in-situ measure of the chemical, elemental and isotopic composition of comet Halley, a neutral MS was employed on the Giotto spacecraft. The instrument consists of two analyzers, one of the double-focusing magnetic sector mass analyzer has a mass range of 1–37 amu [47]. In the late 20th century, several spacecraft loaded with mass spectrometers as well. For example, magnetic sector mass spectrometers were carried on Ulysses and WIND spacecraft launched in the United States to measure ion mass-to-charge ratios and flight times [48].

The European Space Agency's (ESA's) 2003 Mars Express mission include a Beagle 2 lander, the main scientific objectives of the Beagle 2 was to search for organic material on the surface of Mars [49]. The Gas Analysis and Organic Geochemical Package is one of the Beagle 2 configuration, including a single-focusing magnetic MS, the instrument

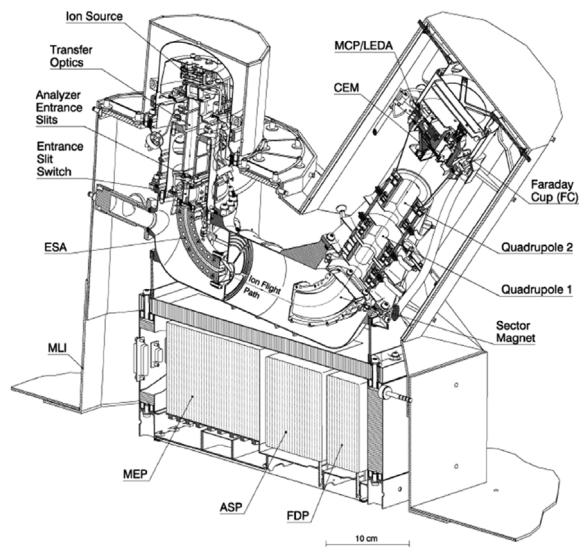


Fig. 5. The three-dimension section view of the double-focusing mass spectrometer. Reprinted with permission from Ref. [51]. Copyright 2007, Space Science Reviews.

mass is 5.5 kg and the power is 60 W [50].

In 2004, a Nier-Johnson double-focusing magnetic sector MS, designed by Balsiger et al. [51], included a  $90^\circ$  electrostatic analyzer and a  $60^\circ$  magnetic analyzer (see in Fig. 5). It has a relative mass resolution of up to 3000, a mass range of 12–100 amu and a sensitivity of  $10^{-5}$  A/Pa. It was carried on Rosetta that launched by ESA in 2004 and was mainly used to analyze the abundance ratio of volatile gases and isotopes around the 67P/Churyumov-Gerasimenko comet [52–54].

The Phoenix spacecraft reached Mars on 25th May 2008, which carried Thermal and Evolved Gas Analysis package (TEGA). The core was a single-focusing magnetic sector MS, it was applied for the analysis of release of volatile substance composition from Martian soil after heating, and proved their corresponding abundance and the isotope ratios of basic elements. Several features of the magnetic sector instrument cause it to be particularly suitable for Mars exploration and to serve as a detector for TEGA. These are simplicity of design, stability, ruggedness, very good mass resolution and the ability to separate small amplitude peaks from adjacent very large amplitude peaks, and minimal electromagnetic interference with other instruments and systems [55]. One of the most important results of this mission was that the presence of icy-soil was found and water was confirmed. It has four mass channels covering the range from 0.7 to 4, 7–35, 14–70 and 28–140 amu, respectively. The magnetic sector MS relative resolution in the highest mass range was 140. The weight of the instrument is 5.7 kg, the size is 24 cm × 23 cm × 18 cm, the power consumption is 13 W. The TEGA instrument is shown in Fig. 6 and the magnetic sector mass analyzer is at the top right corner.

In November 2012, a miniature magnetic sector MS developed by the Lanzhou Institute of Physics was successfully launched with the satellite at the Taiyuan Satellite Launch Center whose main task is to detect the space atmospheric composition [56,57]. The weight of MS is 4.5 kg, the volume is 17 cm × 16.5 cm × 16.5 cm, the power consumption is 18 W, and the sensitivity is  $9.4 \times 10^{-4}$  A/Pa, the absolute resolution of full width at half maximum (FWHM) for  $\text{N}_2^+$  peak is 0.8 amu. The instrument is shown in Fig. 7 (a). Currently the instrument is functioning well in orbit, and the measured results are shown in Fig. 7(b) and (c), from which it can be seen that the detected gas compositions include O, He,  $^{12}\text{CO}_2$ ,  $^{13}\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$ .

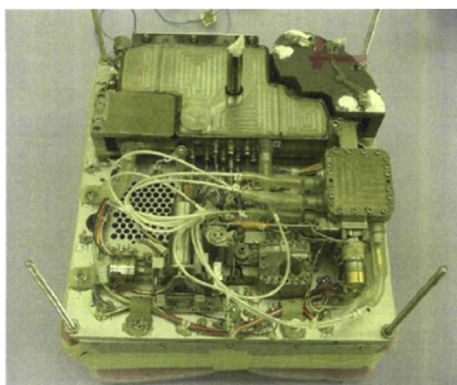


Fig. 6. Complete mass spectrometer package. Reprinted with permission from Ref. [55]. Copyright 2008, Journal of American Society Mass Spectrometry.

### 3. QMS

Quadrupole mass analyzer, also called quadrupole mass filter, is a combination of four parallel cylindrical or hyperbolic electrodes in a square configuration, where the applied radio frequency (RF) voltage signal and direct current (DC) voltage signal (voltage signals have same amplitude and a  $180^\circ$  phase difference) form a quadrupole electric field. A certain mass-to-charge ion passes through the quadrupole field in a stable manner at a certain frequency. When the frequency is changed, the scan for all mass of ions can be achieved. Originally this analyzer was created by Wolfgang Paul in 1953 [58]. The analyzer requires a lower operating pressure than that of the ion trap but higher one than that of the magnetic sector mass analyzer. Because RF amplitude sweeps require a feedback loop to maintain tight linearity, the electronics are complex. Coupled with the stability of the mass selection scan, a high mechanical precision is required. Nevertheless, miniaturized quadrupole mass analyzers have been developed in many fields such as monitoring of atmosphere in the environment, measuring chemicals in foodstuffs, detecting environmental toxins. Especially, it has shown great potential in the field of aerospace applications.

The QMS can adapt to the complicate space environment, and withstand the huge vibration during spacecraft launching. Meanwhile it has advantages of high sensitivity and resolution, wide mass range, good dynamic range, therefore, it has been widely applied in space missions. However, the decrease in the size of the quadrupole analyzer has limited its transmission rate and resolution. The assembly accuracy requirement is strict, where the center distance error of the four rods is in the micrometer magnitude. The smaller the instrument, the tougher

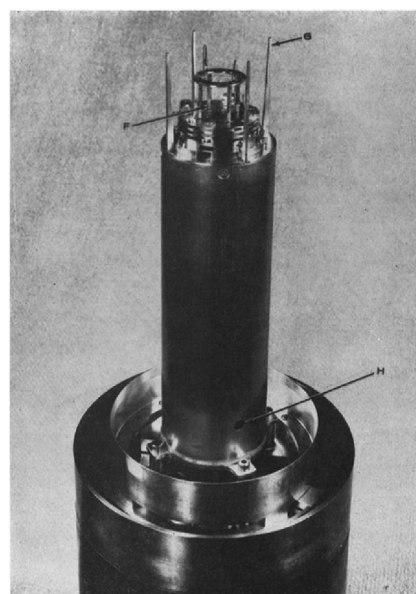


Fig. 8. The photograph of the ion source and mass analyzer end of the instrument package. Reprinted with permission from Ref. [60]. Copyright 1964, J. Geophys. Res.

it is to reach the error of the micrometer magnitude between center distances of the four rods.

The first application of mass spectrometry in space was a QMS that developed at the US Naval Research Laboratory in Washington DC in the late 1950's. Taking into account the influence of various surrounding environmental factors and the better match of the rocket, a QMS employed on the rocket was launched in May 18, 1962 to measure the neutral composition of the upper atmosphere [59,60]. This type of MS is chosen because it can reduce the effects of interaction of the ambient neutral particles and the surfaces of the instrument to the greatest extent possible, it was also required that the instrument be suitable for flight on a small vehicle such as the Nike-Cajun rocket combination [60]. Fig. 8 is a photo of the ion source and mass analyzer packaged. The same MS flown on the Nike-Apache rocket was successfully launched in March 28, 1963 [61]. It mainly measured neutral gas composition at 190 km.

The QMS [62] employed aboard the AE-C, D, and E satellites to measure the neutral thermosphere in-situ. The apparatus is based on the MS carried on Ogo-6 and San Marco-3. The gas density was measured at approximately 125 km–1000 km, the normal operating mode

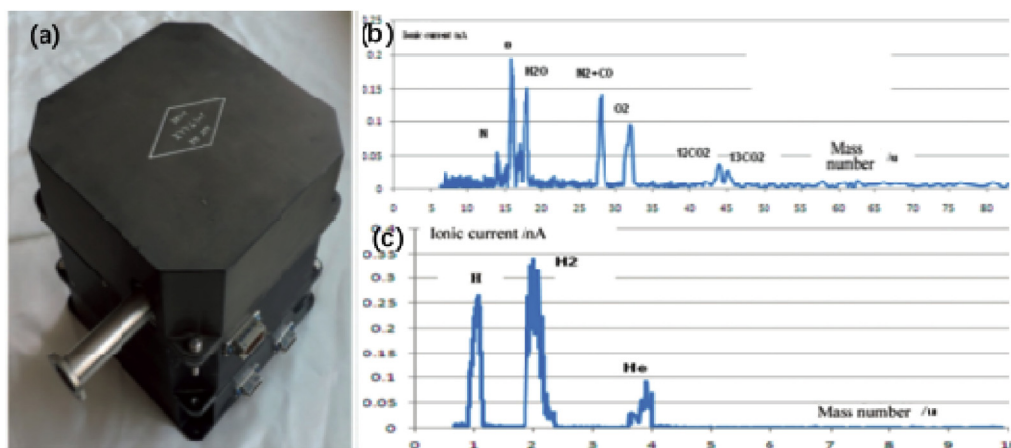


Fig. 7. (A) is the picture of miniature magnetic sector mass spectrometer; (b) is the typical mass spectra obtained from large channel and (c) is from small channel. Reprinted with permission from Ref. [57]. Copyright 2018, European Journal of Mass Spectrometry.

include measurement of all masses in the range 1–44 amu with emphasis on H, He, O, N, and Ar. In addition, Hedin et al. [63] established an empirical model of global thermospheric temperature and composition based on the data of the QMS on Ogo-6. Two years later, Hedin and his co-worker [64] established thermosphere neutral temperatures and N<sub>2</sub> densities model by N<sub>2</sub> density data from mass spectrometers on five satellites (AE-B, Ogo 6, San Marco-3, Aeros A, and AE-C). The QMS also applied to the observation of positive ions of ionosphere. For example, the instrument [65] with a resolution of 16 and a mass range of 1–46 amu flown on the Nike Cajun rocket was successfully launched in October 31, 1963.

To satisfy the measurement requirements of the Dynamics Explorer mission, Carignan et al. [66] developed a neutral gas MS, with a mass range of 22–50 amu. The QMS was used to measure the neutral composition of 300–500 km above the Earth's surface [67].

In 1978, the “Pioneer Venus” detector with the Pioneer Venus Orbit Neutral Mass Spectrometer which is a QMS [68] launched in the United States has a rod length of 7.5 cm, a radius of 0.2 cm and a mass range from 1 to 46 amu. This instrument was used to obtain the neutral gas composition and density in the upper atmosphere (150–250 km above the surface of Venus). Regardless of daytime or nighttime, atomic oxygen was the dominant species above 155 km with a transition to He above 180 km [69]. In addition, there is a “Planet B” neutral gas MS, a double-frequency QMS [70], on the “Pioneer Venus”, which is based on the “Venus” QMS and developed for the purpose of the surface composition detection of the Venus surface. Later, the QMS flown on the Galileo in 1989 [71], used direct leak samples to determine the composition of the Jupiter's atmosphere. The instrument mass range is 2–150amu, the spectrums provided that some of components were possibly PH<sub>3</sub> and Cl.

In 1997, the Cassini spacecraft was launched by the United States, which carried the Huygens Probe and arrived at the Titan atmosphere in January 2005. One of the instruments on board Huygens Probe is GC/MS with the aim of identifying and detecting chemicals in Titan atmosphere [72]. Cassini Ion and Neutral Mass Spectrometer (INMS), the key components of INMS is shown in Fig. 9 [73]. The INMS consists of two ion sources, a quadrupole mass analyzer using the Microsaic system and dual secondary electron multiplier detectors. The main

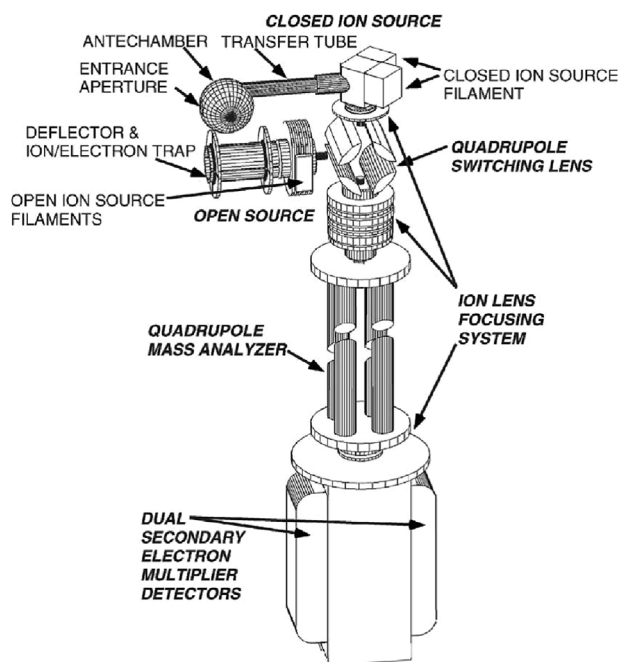


Fig. 9. The key components picture of the INMS. Reprinted with permission from Ref. [73]. Copyright 2004, Space Science Reviews.

**Table 1**  
Space quadrupole mass spectrometers.

Country	Japan	India	USA	India
Prober	Hope Mars	Chandrayaan-1	LADEE	Mangalyaan
Launch date	1998	2008	2013	2013
Mass range	1–60amu	1–100amu	2–20.5amu/ 20.5–150.5amu	1–300amu
Radio frequency	3.25MHz/ 4.85 MHz	–	13MHz/1.4 MHz	–
Rod length	33.7 cm	–	–	–

objective of the INMS is not only to measure the composition of the ionospheric to reveal the relationship between ionosphere and neutral upper atmosphere in the Titan's atmosphere, also to explain the Titan's ionospheric characteristics.

The National Aeronautics and Space Administration (NASA) launched “Curiosity” in June 2011 which then landed on Mars in 5 August 2012, where a quadrupole mass analyzer was carried which can measure light isotopes and volatiles [74]. The presence of chlorobenzene and similar organic on Mars have been confirmed by measurement results [75]. In addition, there are also many probes that carried QMS, summarized in Table 1.

#### 4. TOF MS

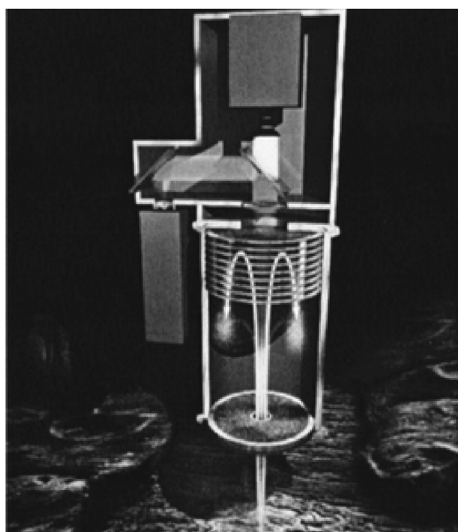
The principle of TOF mass analyzer is that the ions with different mass-to-charge ratios are dispersed in time during flight in a long field free tube of known length. The time for an ion of unknown  $m/z$  in traveling a distance  $s$  after being accelerated by a voltage  $U$  is obtained from equation (2) [25]. All the ions fly at the same time, the detector will receive earlier the mass ratio of lighter ions than the heavier ions.

$$t = \sqrt{\frac{m}{z}} \frac{s}{\sqrt{2eU}} \quad (2)$$

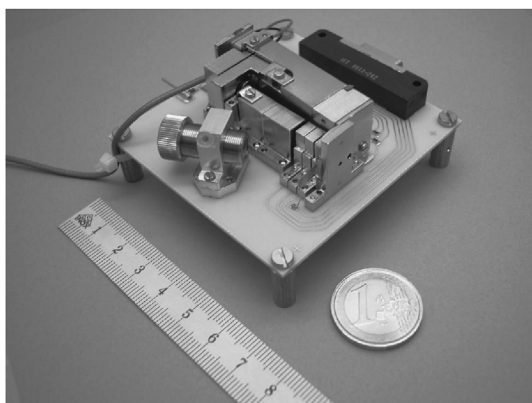
Compared to other mass analyzers, the advantages of TOF mass spectrometers are: wide mass range, high sensitivity, simple structure, especially rapid response, which usually used to quickly analyze comets and other volatile ingredients. However, TOF mass analyzer also has inevitable defects. Its circuits are complex, thus it is often necessary to overcome many difficulties in the process of manufacturing TOF mass spectrometers. The resolution is one of the most important performance indicators of the TOF mass analyzer. Due to the time dispersion, spatial dispersion and energy dispersion of ions before entering the flight tube, therefore, it is difficult to distinguish these ions. That is to say, if the ions with identical mass enter into the flight tube at different time, different location and different speed, then the time of reaching the detector is also different. In order to improve the problem of low resolution caused by time dispersion, spatial dispersion and energy dispersion, the pulsed ion source sampling technique [76] and ion delay extraction technique were employed to greatly improve the resolution of the TOF mass analyzer [77].

Although the resolution and size relationships are not conducive to miniaturization compared to ion trap and quadrupole mass spectrometers, miniaturized TOF MS has yielded good results. Miniature TOF mass spectrometers also have a special appeal in space instrumentation, and elemental analysis is usually performed with laser ablation [78–85]. APL also has been developing a laser ablation MS with a reflection TOF analyzer [86]. Later, the laser ablation TOF MS for space to analysis elemental and isotopic composition of planetary surface was developed by Brinckerhoff et al. [87], the instrument size is very small ( $< 2 \times 10^3 \text{cm}^3$ ) and weight is about 2 kg (see in Fig. 10).

In order to measure the elements and isotopes of Mercury surface solids, Rohner et al. [88] developed the highly miniaturized laser ablation TOF MS, including an electrostatic and a reflection TOF analyzers. The realized prototype instrument is shown in Fig. 11, the



**Fig. 10.** The laser ablation mass spectrometer. Reprinted with permission from Ref. [87]. Copyright 2000, Rev. Sci. Inst.

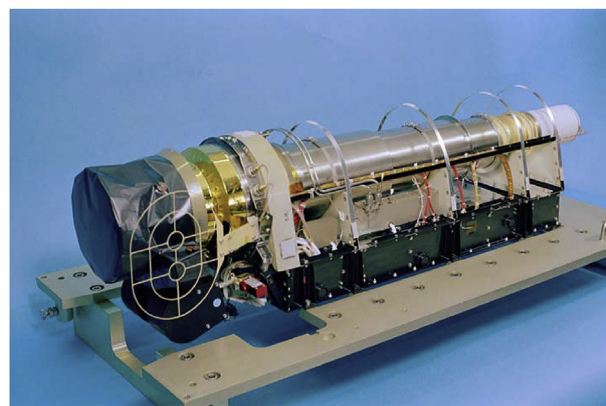


**Fig. 11.** The realized prototype instrument of the laser ablation mass spectrometer. Reprinted with permission from Ref. [88]. Copyright 2004, Rev. Sci. Inst.

instrument was designed to fit BepiColombo mission for the planet Mercury, it weight is 280 g, it consume power is approximately 3 W and have a volume of 84 cm<sup>3</sup> including overall package. Li et al. [89] developed a laser ablation mass spectrometer (LAMS) based on a TOF analyzer, mainly for in situ measurement of the heterogeneous surface compositions of airless bodies. Recently, Moreno-García et al. [90] designed a laser ionization mass spectrometry, which using a miniature RTOF MS, for in-situ analysis of elements and isotopic of solids in space. The mass spectra can be obtained allowing for the clear identification of the parent monomer molecules.

For in-situ analysis of the dust in the universe, Austin et al. [91,92] developed an instrument called Dustbuster, which is a compact impact-ionization TOF MS, suitable for deep space missions. The diameter of the cylindrically symmetric instrument is 10 cm and the length is 20 cm. The TOF MS can be used to analyze the trajectory and size of dust particles with other instruments.

The Cassini Cosmic Dust Analyzer instrument is a linear TOF chemical analyzer with an effective target area of 0.01 m<sup>2</sup> and a relative mass resolution of approximately 50. This is an excellent tool, but the instrument have been power hungry (> 15 W) and massive (> 10 kg), more importantly the target area is small. To detect magnitudes of interstellar dust particles everyday, large target surface areas are needed. Therefore, Sternovsky et al. [93] developed a large-area mass spectrometry instrument for chemical analysis of interstellar dust particles. The



**Fig. 12.** Picture of the RTOF flight spare. Reprinted with permission from Ref. [51]. Copyright 2007, Space Science Reviews.

instrument is a reflection TOF MS that provides a large target area and high resolution compared to previous instruments. In the future the instrument can measure the chemical composition of dust particles in space in-situ.

In space application, the Solar and Heliospheric Observatory (SOHO), launched in 1995, carried a TOF MS to measure chemical elements [94], charges and isotopes to study interplanetary solar winds, hyperthermophilic ions and low-energy particles as well as to measure the mass-to-charge ratio and energy of incident particles. A reflection time of flight (RTOF) MS with detection range of 1–300 amu and resolution of 300 on the Rosetta was used to study the comets [51]. The RTOF flight spare is shown in Fig. 12. RTOF was designed to complement Rosetta double-focusing magnetic sector MS by extending the mass range and increasing the sensitivity of the full instrument package. RTOF instruments have the inherent advantage that entire mass spectra are recorded at once, without the need for scanning the masses through slits. With a storage ion source, high transmission in the TOF section and a sensitive detector, it is possible to record a very large fraction of all ions produced in the ion source. These factors contribute to the superior sensitivity of TOF instruments. Another reason to use them in space science is their simple mechanical design and simple operation. In order to measure the neutral and ion gas components of 67 P comet, two ion sources were adopted in the RTOF: one was Orthogonal extraction ion source which used to measure ion gas components, the other was the Storage ion source which used to measure the neutral gas components of the 67 P. From October 25, 2014 to February 12, 2015, RTOF measured three compounds including H<sub>2</sub>O, CO<sub>2</sub>, and a little CO [95]. The Cometary Sampling and Composition (COSAC) experiment on the “Philae” lander of the Rosetta is focused on analyzing chemical and isotopic composition of 67 P comet, the instrument employed TOF MS with the mass of 2 kg and power of 10 W [96].

## 5. Ion trap MS

Wolfgang Paul first proposed a three-dimensional (3D) ion trap mass analyzer which is a combination of the terminal electrodes with two hyperboloid structures and the ring electrode with one hyperboloid structure in 1950s [58]. The difference between quadrupole and ion trap is that the ion trap mass analyzer is constrained in the z-direction. The miniaturization of ion trap mass analyzer is mainly realized by reducing trap size and simplifying trap structure, the evolution of ion trap analyzer is shown in Fig. 13. At present, the studies of miniaturized ion trap MS mainly focus on cylindrical ion trap and linear ion trap mass analyzers [97].

The Rosetta also employed an ion trap MS (see in Fig. 14) [98], which is the first one applied to space exploration. Ion trap MS is selected because the total payload and physical space available were

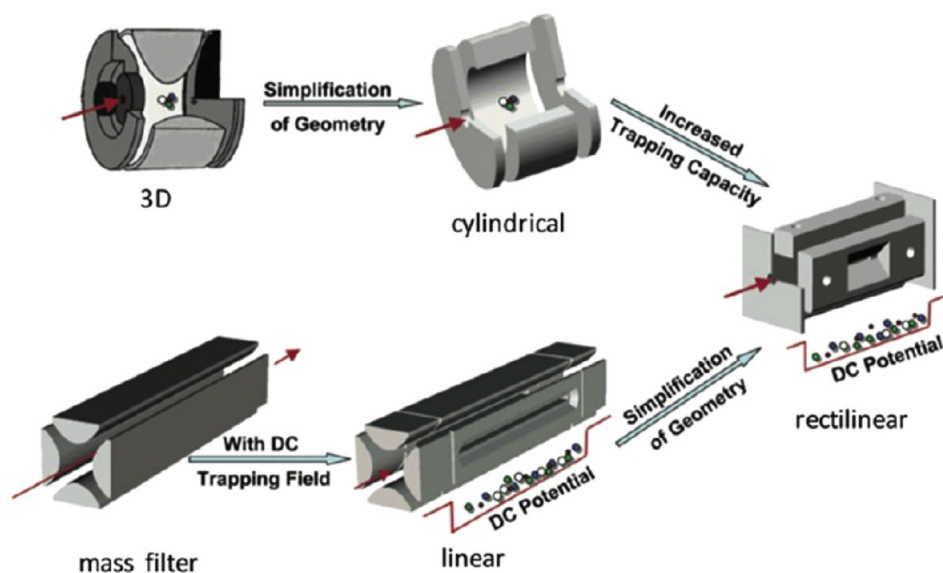


Fig. 13. Evolution of ion trap mass analyzers. Reprinted with permission from Ref. [97]. Copyright 2016, Analytical Chemistry.

severely limited, and given all the other instrumentation being carried by Rosetta and the associated power requirements, alternative analyzer types had to be considered. The small size and simplicity of construction of the ion trap, together with the fact that it functions on the basis of a single parameter control, and that in principle the ion accumulation time can be adjusted in order to allow the build-up of ions from the minor isotopes, thereby increasing the precision of their measurement, made this mass analyzer an obvious candidate for consideration [98]. The instrument can measure accurately the stable isotope ratio of light elements. Its weight is 4.5 kg; the size is 250 mm × 330 mm × 110 mm; the power consumption is 10 W; and the mass range is 12–150 amu. The instrument is not capable to detect the light element like hydrogen directly, but it has adopted an ingenious method to the design, where the sample  $H_2$  was allowed to react with stored  $Ar^+$  to produce  $ArH^+$  and  $ArD^+$ , the ratio of D/H is determined by the  $ArH^+/ArD^+$  [99].

In 2008, one of ESA's Mars exploration programs analyzed the composition of the organic materials on Mars surface by using a low-power miniature quadrupole ion trap MS [100]. The quadrupole ion trap MS as a part of Mars Organic Mass Analyzer (MOMA). The reasons for choosing an ion trap MS are: firstly, it provides the opportunity for MS/MS analysis and it is highly probable that a 2000 amu detection target will be achieved using low voltage and low power; Secondly, it would be more convenient when it is interfaced to an external (Mars)

atmospheric ionization source. The instrument was jointly invested by NASA and ESA to analyze the chemical composition of Mars' surface [101,102].

Of course, the reduction in the size of the ion trap mass analyzer also has some drawbacks. Fewer ions can be trapped ( $10\text{--}10^3$  can be reduced) due to space charge effects, and parameters such as radio frequency and radio amplitude are limited based on physical constrains (i.e. available power and possible discharge) [103]. The manufacture of compact analyzers has also become more difficult because the required absolute tolerances become more stringent. On many occasions, the low mass cutoff increased with decreasing in size, hence the application of the ion trap MS is greatly restricted. However, ion trap mass spectrometers have many advantages in miniaturization. For example, inner diameter of the quadrupole is small, low power consumption because of the low voltage required to analyze the sample at a certain RF frequency. Unlike the fixed relationship between QMS resolution and RF frequency, the resolution of ion trap mass analyzer decreased with increasing in pressure, which is caused by the collision cooling effect. In addition, ion trap MS also has advantages in measuring the large mass of organic compounds and other large mass gas in space, it is convenient to connect with the external atmosphere ion source and MS/MS analysis. With the deep space exploration of biological protein molecules, ion trap MS has a wide application prospect in the future.

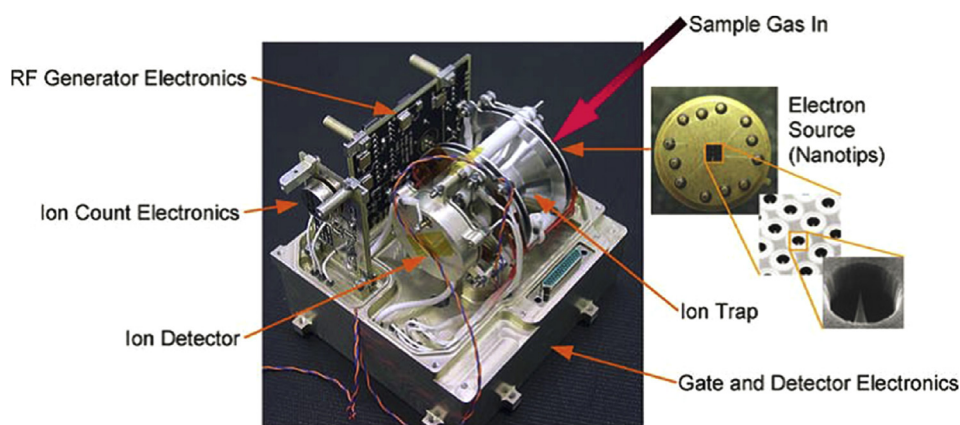


Fig. 14. Schematic diagram of the ion trap mass spectrometer installed onboard ROSETTA spacecraft. Reprinted with permission from Ref. [99]. Copyright 2007, Space Science Reviews.

## 6. Conclusion and expectations

Up to now, the researches and applications of space miniaturized mass spectrometers have been studied for decades. The capabilities and applications of the MS have been gradually spread from the ionosphere to the outer atmosphere, extended into the deep space of the Lunar, Jupiter, Mars, and asteroids. Mass spectrometers based on magnetic sector, quadrupole, ion trap, and TOF mass analyzers have applied in space. The main scientific objectives include measuring atmospheric composition and positive ions at different altitudes, as well as landing on the surface of the planet to determine the components of local atmosphere, soil, and rock. Quadrupole is widely used and is also the earliest applied MS in space exploration. It has good quantitative ability, low requirement for working vacuum, easy to implement, light weight. Followed by magnetic sector MS, the instrument with high resolution, simple structure, good stability, widely used in various tasks. However, if shrink in the volume and weight of the magnet greatly affects the strength of the magnetic field, as a result its analytical performance is decreased. Ion trap and time-of-flight mass spectrometers have advantages in the analysis of large-molecules components. With the development of deep space exploration, deep space missions are also necessary for the detection of some biological protein molecules.

Presently, how to make the mass spectrometers easy to carry and use for its application in space is a cutting-edge issue that are concerned by researchers without loss of performance. In addition, it is necessary to select different types of MS which is most suitable to meet the different space scientific objectives. Although different types of mass spectrometers have been employed successfully, the target of detection is constantly changing with the further development of space exploration. In the future, I think MS will mainly be studied in the following three aspects:

- (1) MEMS technique is becoming attractive as a mature processing technique. It can produce all kinds of products with small volume, light weight, low power consumption and excellent performance. MEMS technique is relatively mature on the ground MS [104–108]. But there was no miniature MS produced from MEMS technique in space exploration. In recent years, some scientists have been developing space MEMS mass spectrometers in the laboratory. For instance, Van Amerom et al. [109] manufactured  $\mu$ -cylindrical ion trap mass spectrometers for chemical analysis in space using MEMS technique. The performance of each of the 54  $\mu$ -CITs in the array was individually investigated using a rasterable electron gun to ionize gas molecules inside each trap. Zheng et al. [110] developed a micro Cylindrical Ion Traps ( $\mu$ CIT) for CubeSats and NanoSats Application by MEMS technique. The size of the assembled  $\mu$ CIT is only 12 mm 2 mm 1.5 mm. It contains 44 array. Besides, MEMS mass spectrometers have studied by others [111,112]. In the future, MEMS technique will promote the rapid development of space exploration MS and the MS continue to play an important role in space field.
- (2) The MS can only analyze the space gas composition at the present. With the development of deep space science, the phase of the examine material also changes. If new ionization techniques such as inductively coupled plasma, laser ionization, threshold ionization, and electron trapping ion sources are based on ground instruments, solids can be ionized to detect in space. For example, laser ablation combined with TOF instrument is used to detect dust particles in the space [78–90]. There is no doubt that the applications of ionization technology combined with mass spectrometers in space are also very advantageous in the future.
- (3) Mass analyzer must have the characteristics of small size, light weight and low power consumption, but the scale-down of space miniature MS is not confined to the miniaturization of mass analyzer, reducing the vacuum system, sample system and power

supply are also imperative. For example, the mass spectrometer's pump system can be reduced, the circuit part of the MS can be made as small as possible, and the support system of the MS should be considered.

## Acknowledgment

The authors would like to acknowledge the support of GanSu Province Major Science Technology Projects (NO.17ZD2WA001) and the National Natural Science Foundation of China (Grant NO.61671226, 61471184, 61627805, 61771228 and 61701210).

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.vacuum.2018.05.048>.

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