Analysis on Mars Atmospheric Composition Probing Technology in the Future

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Abstract. Mars atmospheric composition probing is one of critical tasks of mars exploration. The mars atmosphere may have the existence of water, methane, organic matter, conducting mars atmospheric composition probing is very critical to studying whether the mars has, or once had the existence of living matter, analyzing the forming, evolution of mars atmosphere as well as its change with season. Restricted by launching technology, platform technology, mars exploration task has very strict requirement to weight, volume and power consumption of probing load. At present, the mars atmospheric composition in-situ probing load in abroad usually adopts mass spectrometry with load weight from several kilogram to tens kilogram, and power consumption from several watts to tens watts. Carbon Nanotubes (CNTs) has large surface area with sensitivity to gas absorption reaction, and can be used to prepare the high performance gas sensor with high sensitivity, quick response, light weight, small volume, and low power consumption, and it is possible to realize atmospheric composition probing load with 100g weight and milliwatt power consumption. CNTs gas sensor technology shall be the critical development trend of mars atmospheric exploration technology in the future.

1. Introduction
Mars exploration is an important field of global spaceflight activity at present. For a period of time in the future, the trend of mars exploration shall be inclined to probing of living matter. According to near term launching and future planned launching of deep space probes in abroad, its main objective is to study whether the mars has the existence, or once had the existence of living matter, while mars atmospheric composition in-situ probing load is one of main means to realize this objective.

The mass spectrometer is an important gas analytical instrument and has played a critical role in mars exploration task already conducted. Nevertheless, with gradual development of scientific understanding and development of basic technology, like micro-electronics and new type material, the probing load gradually develops towards light and small type, long service life, high reliability, and high integration. The load function is gradually increasing, while the weight and power consumption is gradually decreasing, and this is an important direction of mars probing load technical development in the future. Therefore, the atmospheric composition probing load on the basis of a new type technology may distinguish itself in mars atmospheric in-situ probing in the future.

On the basis of analyzing Mars atmospheric composition probing load in abroad, this paper focuses on development and application of new technology, researches the application of CNTs gas sensor in Mars atmospheric composition probing, and discusses the technical bottleneck of carbon nano tube gas transducer.
2. Analysis on mass spectrometer for superior planet atmospheric composition probing

According to difference of scientific probing goals and probing objects, and impact of load volume, weight, power consumption, sensitivity, resolution, at present the mass spectrometer for probing planetary atmospheric composition mainly includes magnetic deflection mass spectrometer, quadrupole mass spectrometer, time of flight mass spectrometer, ion trap mass spectrometer, and they were all once used for planetary atmospheric composition probing.

2.1. Magnetic deflection mass spectrometer

Viking 1 and Viking 2 launched in 1976 adopted the uniform structure magnetic deflection spectrometer to analyze surface atmosphere of Mars[1]. The mass spectrometer was of Nier-Johnson structure, with one electron impact ion source of sensitivity $10^{-8}$/pa, and one double focusing mass analyzer. The instrument weight was 10kg, ion mass number probing range was 1~230amu.

The Phoenix Mars Lander, which arrived at Mars in 2008, carried a thermal evolved gas analyzer TEGA, the core of lander was a magnetic deflection mass spectrometer for analyzing volatile substance content after heating the soil of Mars, and determining main composition of Mars atmosphere[2]. The structure of mass spectrometer was shown in Fig.1. The weight of mass spectrometer was 4.3kg, mean power consumption was 13W, the magnetic analyzer included four channels with related mass number range 0~14amu, 7~35amu, 14~70amu, 28~140amu.

2.2. Quadrupole mass spectrometer

Galileo Jupiter Probe, which was injected into Jupiter orbit in 1989, carried the quadrupole mass spectrometer[3]. The weight of mass spectrometer was 13.2kg, mean power consumption was 13W. The mass number measurement range of mass spectrometer was 2~150amu, and the resolution was higher than 1ppb. Accuracy of He partial pressure proportional measurement was 1%, accuracy of H$_2$O, CH$_4$, NH$_3$ partial pressure probing was 5%.

The Huygens Probe of Saturn also carried quadrupole mass spectrometer to measure the Titan atmospheric composition[4]. The mass spectrometer of Huygens Probe adopted the aspirator pump and an ion sputtering pump to maintain cleanliness of vacuum chamber. The weight of mass spectrometer was 17.3kg, mean power consumption was 28W, mass number measurement range was 2~150amu, mass resolution was $10^{-6}$ for 60amu.

2.3. Time of flight mass spectrometer

The Rosetta Spacecraft, which was launched by ESA in 2004, carried a test pack ROSINA[4]. The test pack was fitted with a time of flight mass spectrometer to detect the organic matter as polycyclic
aromatic hydrocarbon carbohydrate. The structure of mass spectrometer was shown in Fig. 2. The weight of mass spectrometer was 15kg, mean power consumption was 30W, mass number measurement range was 1~300amu.

Figure 2 The structure of Time of flight mass spectrometer

2.4. Ion trap mass spectrometer
The Rosetta Spacecraft of ESA was also fitted with an ion trap mass spectrometer to probe the gas with mass number 1~150amu.

In the design of Extraterrestrial Mars Program of ESA, the Mars organic mass analyzer (MOMA) shall be carried, its core is an ion trap mass spectrometer. The mass number probing range can be extended to 2000amu, and it can be used to probe the organic matter with high molecular weight.

At present the weight of various mass spectrometers ranges from several kg to tens kg, power consumption from several watts to tens watts, and they are mainly used to probe the gas molecule with small mass number. The mass spectrometer is also confronted with some technical bottlenecks for Mars atmospheric probing. The development and application of some latest technologies is hopeful to surpass mass spectrometer to greatly improve the technical level of Mars atmospheric probing.

3. Introduction of CNTs gas sensor
In 1991, Iijima the scientist of NEC Company of Japan found a new carbon structure [5], as shown in Fig.3.

Figure 3 The structure of CNTs

The electrical property of CNTs seriously depends on outermost layer carbon atom, after combination of external layer carbon atom with gas molecule, electrical property of CNTs may change, therefore CNTs can be used as gas sensor to probe ppm (1/10^6) and even ppt (1/10^12) concentration.
gas[6,7]. CNTs sensor can be sorted as semiconductor sensor for spatial atomic oxygen detection, in contrast with existing atomic oxygen detector. It is featured by quick response speed, high sensitivity, small volume, low power consumption, high accuracy, and has a huge technical advantage. At present AMES research center of NASA of USA has manufactured 32 channel CNTs sensor unit for some satellite of USA navy, for detecting NO₂ concentration[8] of orbit, and realizing spatial application of CNTs sensor.

3.1. Working principles of CNTs gas sensor
The traditional gas sensor is a gas sensor that causes a change in the physical and chemical properties of the sensor unit after contact with the sensitive unit of sensor, and reacts to the output of the electrical signal to be determined by the change in the size of the electrical signal.

CNTs gas sensors can be divided into resistor/conductivity type and capacitor type according to the different electrical signals detected. At present, the most majority of CNTs gas sensors analyze gas concentrations by measuring changes in resistance/conductivity of CNTs[9].

As shown in Figure 4, when the gas molecules under test are adsorbed on the surface of the CNTs, the resistive/conductivity regularity of the CNTs will be changed, thereby detecting the gas composition and content.

![Figure 4](image_url)

**Figure 4** Representative sensor response for NO₂[9]

3.2. Performance of CNTs gas sensor
The main performance parameters of CNTs gas sensor include:
- Sensitivity-the minimum content of gas that can be detected;
- Response time-the time from start of gas environment change to stabilization of electrical signal change of sensor;
- Recovery time- the time from eliminating environment of gas under detection, to the time when the electrical performance of sensor is recovered to original value;
- Selectivity- the sensor only has response to certain category gas without response to other gases.

This property determines whether the sensor can be used for probing the mixed gas consisting of multiple gases.

Carbon nanotubes used in CNTs gas sensor can be divided into two major categories, they are pristine carbon nanotubes and functionalized carbon nanotubes. Pristine carbon nanotubes sense gases by the properties of pristine carbon atoms on the surface of carbon nanotubes Functionalized carbon nanotubes are prepared by chemical or physical modification. Their surface carbon atoms are combined with other atoms or molecules to function.

Pristine CNTs gas sensor has the following disadvantages: poor selectivity, low sensitivity and the response time and recovery time are long.
Many gases can influence the electrical properties of pristine carbon nanotubes. Therefore, when the CNTs sensor is exposed to a mixture of unknown components, the sensor will respond, but it can not distinguish these gases and can not determine the concentration of the gas. Even under the known main gas composition conditions, the gas concentration can not be accurately judged. The sensitivity of carbon nanotubes to different gas varies greatly, ranging from ppb level to more than 100 ppm level. Even if the same gas is detected, the results obtained by different research teams are also different. It shows that the sensitivity of the sensor has a great relationship with the preparation process of the carbon nanotube sensor and is not easy to control. In practical applications, ppt level gas concentrations need to be detected. The performance of sensors should be relatively stable. Pristine CNTs sensor is not enough to meet such requirements.

For most gases, the response time and recovery time of the carbon nanotube sensor are relatively long, taking several minutes or even ten minutes. For certain gases, the performance of the pristine carbon nanotube should not be fully restored, and the sensor should not be reused.

Functionalized CNTs gas sensor can detect more kinds of gases. The performance indexes such as sensitivity, response time, recovery time, and selectivity are superior to those of pristine carbon nanotubes. Therefore, this kind of sensor has more practical application value. A more effective method at present is to functionalize the surface of the CNTs with atoms, molecules, functional groups. The functional combination of CNTs is divided into two types: covalent bonding and non-covalent bonding.

4. Analysis on feasibility of applying CNTs gas sensor to mars atmospheric composition probing

4.1. Feasibility analysis

For mars atmospheric probing, the main probing objective gas includes CO$_2$, H$_2$O, CH$_4$ and organic molecule, etc. While CNTs sensor has realized detection to such gas, e.g., CH4 with available detection concentration 6ppm, ethyl alcohol, glucose, etc. Furthermore, according to requirement of objective gas under probing, more gas probers can be developed. Therefore, CNTs sensor is hopeful to realize probing of objective gas of mars.

4.2. Analysis on challenge of technology

The mars atmosphere has multiple gases which may all influence electrical signal of sensor, therefore the sensor must have fairly strong selectivity, during design and manufacturing of CNTs sensor, CNTs shall be specially treated so that electrical property of CNTs shall only respond to certain gas composition instead of other gases. The CNTs sensor with different gas selectivity shall be integrated into a chip to recognize the gas category and content in the mars atmosphere. Performance index of CNTs gas sensor shall be further improved in accord with mars atmospheric probing requirement, although CNTs gas sensor has very high sensitivity to some gas perception and detection, sensitivity of CNTs gas sensor is not yet ideal for most gases. The mars atmosphere has a variety of gas contents, wherein, some gas has extremely low content and shall not be detected until the sensor has fairly high sensitivity. Therefore, according to mars atmospheric probing objective, high performance gas sensor shall be researched and manufactured, to improve perception capability of sensor to gas via certain CNTs functional method.

Researching CNTs gas sensor performance in the lab is usually conducted at room temperature. The environment condition is fairly simple, while mars atmospheric environment differs greatly from lab environment, the atmosphere mainly includes CO$_2$ with high, low temperature environment and radiation environment, etc. The influence of these environmental factors to CNTs sensor is still unclear. Environment effect research of sensor is almost a blank, therefore sensor environmental adaptability research and protection design research shall be enhanced to resolve the environment problem of CNTs gas sensor engineering application.

The current created of CNTs gas sensor is only microamp level and power consumption microwatt level, but the electrical signal measurement, treatment system as well as data transmission system may
greatly increase the weight and power consumption of mars atmospheric probing load system. Therefore, the system design shall be optimized in accord with electrical signal characteristic of CNTs sensor to realize light and small type orientation of the whole system.

5. Conclusion
The mars atmosphere in-situ probing is one of important constituted parts of mars exploration in the future. The deep space probing has strict requirement to dimension, weight and power of probing load. Although various mass spectrometers have plenteous performances for planetary atmospheric probing, the miniaturization, low power consumption and high performance of mass spectrometer shall be further improved to satisfy the requirement of deep space exploration. CNTs gas sensor has the advantages of high probing sensitivity, quick response speed, a variety of gases under probing, small volume, low power consumption, simple structure, batch production, low cost. Therefore CNTs gas sensor shall be the ideal probing load for mars atmosphere in-situ probing in the future.

References
[1] Biemern K, Oro J, Toutrin P. J. Geophys. Res, 1977, 82:4641-4658
[2] John H. Hoffman, Roy C. Chaney, Hilton Hammack. Phoenix mars mission-The thermal evolved gas analyzer. J. Am. Soc. Mass Spectrom, 2008, 07:15
[3] Theresa Evans-Nguyen, Luann Becher, Vladimir Doroshenko, Robert J. Cotter. Development of a low power, high mass range mass spectrometer for mars surface analysis. International journal of mass spectrometry. 2008, 278:170-177
[4] Chicarro A, Clavel J, Escoubet C P, Favata F, Foing B, Fridlund M, Gimenez A. ESA’s Report to the 35th COSPAR Meeting. Paris, France. July, 2004
[5] S.Iijima. Helical microtubules of graphitic carbon[J]. Nature,1991,354 pp. 56-58.
[6] P.Qi, O.Vermesh, M.Grecu, et al. Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection[J]. Nano Lett.,2003, vol. 3, pp. 347–351.
[7] Snow E R, Perkins F K, Robinson J A. Chemical vapour detection using single-walled carbon nanotubes. Chemical Society Reviews, 2006, vol. 35, pp.790-798.
[8] http://www.nasa.gov/centers/ames/home/index.html.
[9] Li P F, Martin C M, Yeung K K et al. Dielectrophoresis aligned single-walled carbon nanotubes as pH sensors. Biosensors, 2011 vol.1, pp.23-35.