Development of the portable mass spectrometer and its application in environmental monitoring

Guo Cuilian¹, Cheng Yongqiang¹,*, Liu Maoke¹, Zhao Bin¹, Zhang Shuwei¹, and Zhang Li¹

¹ Institute of Oceanographic Instrumentation, Qilu University of Technology (Shandong Academy of Sciences); Shandong Key Laboratory of Ocean Environmental Monitoring Technology, Qingdao City, Shandong Province, 266001, China

Abstract. We reviewed the current key techniques of portable mass spectrometer and discussed its application in environmental monitoring. At present, mass spectrometer has two development directions. One direction is high-throughputs, high-sensitivity and high-resolution laboratory mass spectrometer. The other is small, in-situ monitoring portable mass spectrometer. With the rapid development of electronic technology and new materials, portable mass spectrometers are widely used in environmental pollution monitoring because they have the advantages of small size, light weight and low power consumption.

1. Introduction

With the rapid development of economy, the environment is facing increasing pressure. The problems of environmental pollution are unprecedented, such as smog and haze, water eutrophication, volatile organic compounds (VOCs), heavy metal pollution, acid rain pollution. In the process of routine environmental monitoring, samples are usually taken back to the laboratory for analysis. However, the sample compositions may change due to the influence of pressure, temperature or other conditions in the process of sampling and transportation, which is difficult to ensure the accuracy and effectiveness of environment contamination analysis. Rapid qualitative and accurate quantification of pollutants in the field is a critical problem that needs to be solved all the time[1-3]. In recent years, portable mass spectrometers have attracted wide attention due to their high sensitivity, fast analysis and wide application[4-6]. Sample injection system, the ion source and mass analyzer are three key techniques for portable mass spectrometers, which ensure the wide application in the field of environmental monitoring.

1.1. Sample introduction system

Mass spectrometer runs under high vacuum condition, while the sample is under atmospheric pressure. It is one of key techniques of portable mass spectrometer for how to put the sample from atmospheric pressure to high vacuum mass spectrometer[7, 8].

Direct introduction method is usually used by a capillary, which is applied as the portable gas chromatography-mass spectrometry (GC-MS) interface. The portable GC-MS is commonly used to qualitatively identify and quantitatively detect complex organic chemical components[9, 10]. The capillary carries gas flow rate at 1 to 2mL/min with inner diameters between 0.25mm and 0.32mm. The carrier gas and the sample are introduced directly into the ion source of the mass spectrometer. The sample is measured after being ionized into charged particles while the carrier gas is pumped away because it is an inert gas and cannot be ionized. The direct introduction method has advantages of simple structure, easy to maintain and high transmission rate. This method is optimal choice for identifying and quantifying volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), toxic industrial materials (TIMs), chemical warfare agents (CWAs), and toxic industrial chemicals (TICs)[11, 12].

Representative instruments on the market today include HAPSITE® ER, TORION, Mars-400, Griffin 460 and Agilent 5975T.

In order to simplify the system structure, Yu et al.[13] used capillary introduction mass spectrometer to detect the sample without the separation process of gas chromatography. The results indicated that it was capable of performing direct analysis of liquid when a 5-µm capillary was used as the sampling interface. Meanwhile, the capillary flow rate is limited by the mass spectrometer vacuum pump. The vacuum of the mass spectrometer increases and the sensitivity decreases when the flow rate is beyond the rated value.

In 1963, G. Hock et al.[14] firstly combined membrane introduction technique with mass spectrometry to detect dissolved gas in water. Membrane introduction mass spectrometry (MIMS) was originally used to monitor dynamic chemical samples[7]. Since its development, MIMS for chemical analysis involves directly sampling analytes in gaseous, liquid and solid samples through a semi-permeable membrane[4, 15-17]. Polydimethylsiloxane (PDMS) is the most frequently selected membrane for MIMS analysis of the volatile...
organic compounds. The sample can quickly penetrate into the membrane and enrich in organic molecules due to the selective permeation properties of the membrane. However, the inorganic substances such as H₂O, N₂, O₂ are hard to penetrate into the membrane. In addition to having good permeability, the membrane must have high mechanical strength. Miranda et al.[18] fabricated a polysiloxane nano-composite (PNC) membrane, which was used to minimize compression effects and provide better linearity responses than PDMS membrane.

Since MIMS is an on-line analytical technique, in which samples can be continuously flowed over the membrane interface, it can yield analytical results in real time without the need for sample clean-up and chromatographic separation[19]. MIMS can provide simplicity, high-speed and high-sensitivity, and are suitable for measurement of complex matrices[20]. At present, Various membrane introduction systems based on different structure arrangements including cryotrapping-MIMS (CT-MIMS)[21], purge-and-membrane mass spectrometry (PAM-MS)[22], trap and release-MIMS (T&R-MIMS)[23], laser desorption-MIMS (LD-MIMS)[24] were developed. VOCs or semi-VOCs in various matrixes, particularly in aqueous matrixes, were analyzed efficiently in portable mass spectrometers.

2. Ion source

Ion source is the key component of portable mass spectrometer, and it is important to provide a standard matching small ion source for the substance to be measured.

Detecting VOCs or SVOCs in the atmospheric environment, electron beam bombardment ionization (EI) ion source is commonly applied in the portable mass spectrometer. The ion source temperature is set to ~100 °C, and the electron filament energy was 70 eV. EI ion source has the advantages of simple structure and referential available database, and it has been used in many commercial instruments. However, EI ion source need low vacuum degree requirements and it can produce a lot of fragment ions because 70 eV is higher than the ionization energy of the compound. Moreover, the fragment ions will cover the ion peak to be measured, which reduces the analysis sensitivity. In order to ensure the accuracy of measurement, it commonly needs to be combined with pre-separation technique such as gas chromatography[25].

Photoionization ion source is also a promising technique to portable mass spectrometer due to its stable performance, low vacuum requirement, long working life[26-28]. Hou et al.[29] developed an ultraviolet photoionization (UVP) ion source which ionized the organic compounds in atmospheric environment. The UVP ion source with photon energy 10.5eV is a soft ionization source to form only parent ions without fragment ions for most organic compounds, so the mass spectrum can easily be identified without prior separation. Recently, Proton transfer reaction (PTR) ion source has attracted people’s attention, which will be an important technique to detect trace amounts of VOCs in atmospheric environment[30-32]. PTR-MS can detect the absolute concentration of VOCs within several minutes and consequently the real-time monitoring VOCs changes[33]. PTR-MS has many advantages including high sensitivity, no need for pretreatment, easy operation, and short response time. However, it is difficult to carry out the qualitative analysis of unknown compounds by PTR-MS, which can only be speculated based on the distribution of fragment ions of standard substances, relevant literature reports and the detection results.

3. Mass analyzer

In-situ environmental monitoring is the application target of portable mass spectrometer, so the mass analyzer must be miniaturized. Linear quadrupole, ion trap, magnetic sector, time-of-flight, and cycloidal mass analyzers are the types of mass analyzers that have been miniaturized successfully so far[34-36]. At present most portable mass spectrometers employ linear quadrupole mass analyzers which are compact, low-cost and robust. Ion traps have also usually been used in the portable mass spectrometers, which are especially useful in environmental and trace monitoring because they are higher sensitive and wider mass range than linear quadrupole mass analyzers. In recent years, time-of-flight mass analyzers have been widely used in online monitoring of environmental toxic organic pollutants[37-39], which have many advantages including wide mass range, fast response speed, high resolution, high sensitivity. Meanwhile, time-of-flight mass analyzers are easy to be processed and miniaturized and the potential mass analyzers for on-line monitoring organic pollutants.

4. Conclusion

The development of the portable mass spectrometers is being accelerated with the requirement of in-situ environmental monitoring and the improvement of fabrication technologies. But so far it is an important limitation that current portable mass spectrometers are not universally suitable for large groups of users. They are still individually custom-built for specific environmental pollutants. In the future, we expect that the highly sensitive and versatile portable mass spectrometers will be further developed and they can be widely used in the field of environmental monitoring.

Acknowledgement

Financial supports from Natural Science Foundation of China (No. 21207080), Natural Science Foundation of Shandong Province (No. ZR2011BQ021), Outstanding youth training program of Shandong academy of sciences (No. YJQ303), National Key Technology R&D Program of the Ministry of Science and Technology (2012BAF14B04), the National Key R&D Plan (No. 2016YFC1400800) are gratefully acknowledged.
References
1. Brennwald MS, Hofer M, Kipfer R. Environmental Science & Technology 47, 8599-8608 (2013)
2. Tyroller L, Tomonaga Y, Brennwald M, Ndayisaba C, Naeher S, Schubert C, North RP, Kipfer R. Environmental Science & Technology 50, 7047-7055 (2016)
3. Overton EB, Dharmasena HP, Ehrmann U, Carney KR. Field Analytical Chemistry & Technology 1, 87-92 (2015)
4. Brennwald MS, Schmidt M, Oser J, Kipfer R. Environmental Science & Technology 50, 13455 (2016)
5. Mehl L, Brennwald MS, Kipfer R. Environmental Science & Technology 46, 8288-8296 (2012)
6. Vautier C, Chatton E, Abbott B, Harjung A, Labasque T, Guillou A, Pannard A, Piscart C, Laverman A, Kolbe T. Egu General Assembly Conference (2017)
7. Davey NG, Krogh ET, Gill CG. Trac Trends in Analytical Chemistry 30, 1477-1485 (2011)
8. Johnson RC, Cooks RG, Allen TM, Cisper ME, Hemberger PH. Mass Spectrometry Reviews 19, 1-37 (2000)
9. Zhang X, Cheng L, Ke W, Yang G, Yang L. China Resources Comprehensive Utilization (2016)
10. Nikonova AA, Gorkhov AG. Analytical Letters 44, 1290-1300 (2011)
11. Eckenrode B. J Am Soc Mass Spectrom 12, 683-693 (2001)
12. Eckenrode BA. Field Analytical Chemistry & Technology 2, 3-20 (2015)
13. Quan Y, Kai N, Fei T, Xiaohao W. Chinese Journal of Analytical Chemistry 41, 1287-1290 (2013)
14. Hoch G, Kok B. Archives of Biochemistry & Biophysics 101, 160-170 (1963)
15. Chatton E, Labasque T, de la Bernardie Jm, Guihéneuf N, Bour O, Aquilina L. Environmental Science & Technology 51, 846-854 (2017)
16. Schenk HJ, Espino S, Visser A, Esser BK. Plant Cell & Environment 39, 944-950 (2016)
17. Mendes MA, Sparrapan R, Eberlin MN. Analytical Chemistry 72, 2166 (2000)
18. Miranda LD, Bell RJ, Short RT, Amerom FHWV, Byrne RH. Journal of Membrane Science 385, 49-56 (2011)
19. Soni M, Bauer S, Amy JW, Wong P, Cooks RG. Analytical Chemistry 67, 1409-1412 (1995)
20. Johnson RC, Cooks RG, Allen TM, Cisper ME, Hemberger PH. Mass Spectrometry Reviews 19, 1-37 (2015)
21. Mendes MA, Pimpim RS, Kotiaho T, Eberlin MN. Analytical Chemistry 68, 3502-3506 (1996)
22. Ojala M, Poutanen M, Mattila I, Ketola RA, Kotiaho T, Kostiainen R. Rapid Communications in Mass Spectrometry Rcm 14, 994-998 (2000)
23. Mendes MA, Eberlin MN. Analyst 125, 21-24 (2000)
24. Soni MH, Callahan JH, Mcelvany SW. Analytical Chemistry 70, 3103-3113 (1998)
25. Santos FJ, Galceran MT. Journal of Chromatography A 1000, 125-151 (2003)
26. Shizuma K, Hideo Y, Minoru D, Satoshi S, Shigenori T, Hiroshi F, Shigeki M. Analytical Chemistry 77, 1007-1012 (2005)
27. Hanley L, Zimmermann R. Analytical Chemistry 81, 4174-4182 (2009)
28. Jiang J, Wang Y, Hou K, Hua L, Chen P, Liu W, Xie Y, Li H. Analytical Chemistry 88, (2016)
29. Hou K, Dong C, Zhang N, Xu X, Wang J, Lian Y, Chai Z, Anyang Chinese Journal of Analytical Chemistry 34, 1807-1812 (2006)
30. Zhang QL, Zou X, Liang Q, Zhang YT, Y MJ, Wang HM, Huang CQ, Chen CY, Chu YN. Chinese Journal of Analytical Chemistry 46, 471-478 (2018)
31. Kang M, Zou X, Lu Y, Wang H, Shen C, Jiang H, Chu Y. Chemical Research in Chinese Universities 32, 565-569 (2016)
32. Hayeck N, Maillot P, Vitrani T, Pic N, Wortham H, Gligorovski S, Temime Roussel B, Mizzi A, Poulet I. Metrology, Inspection, & Process Control for Microlithography (2014)
33. Chengyin S, Jianquan L, Hongzhi W, Zhonghua Z, Hongmei W, Chaoqun H, Sheng L, Haihe J, Yannan C. Chinese Journal of Analytical Chemistry 40, 773-777 (2012)
34. Badman ER, Graham CR. Journal of Mass Spectrometry 35, 659-671 (2015)
35. Chua EJ, Savidge W, Short RT, Cardenas-Valencia AM, Fulweiler RW. Frontiers in Marine Science 3, 1-24 (2016)
36. Kogan VT, Pavlov AK, Chichagov YV, Tuboltsev YV, Savchenko MI, Smirnov OB, Viktorev OS, Viktorov IV, Vlasov SA, Dubenski BM. Technical Physics 52, 1604-1610 (2007)
37. Tan GB, Mai ZB, Yu JJ, Mei L, Huang ZX, Cheng P, Zhou Z, Gao W. Journal of Chinese Mass Spectrometry Society (2016)
38. Li N, Xu H, Li Q, Wang Y, Xing J, Xu X. Spectroscopy Letters 45, 464-469 (2012)
39. Zhou Z, Yu JJ, Huang ZX, Xue L, Mei L, Lei L, Tan GB, Mai ZB, Gao W. Chinese Journal of Analytical Chemistry 43, 783-787 (2015)