Influence of focusing voltage on sensitivity of quadrupole mass spectrometer

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Abstract. Sensitivity is an important performance parameter of the quadrupole mass spectrometer. The ion source parameters, quadrupole parameters and collector parameters of the quadrupole mass spectrometer all affect the sensitivity of the mass spectrometer, and the focusing voltage of the ion source is a core factor. In this paper, the theoretical analysis of the electromagnetic field of the focusing voltage is carried out. The relationship between the focusing voltage and the sensitivity is simulated by using SIMION software. And the simulation results are verified by experiments. Finally, the proposed method is proposed to improve the sensitivity of the mass spectrometer by adjusting the focusing voltage.

1. Introduction
Quadrupole mass spectrometer (QMS), as the most widely used mass spectrometer, has some performance indexes, such as sensitivity, relative sensitivity, quality calibration, pattern coefficient and linearity. Generally, these parameters of the QMS are not independent of each other, and it is impossible to make the best performance parameters [1]. In the actual partial pressure measurement, its performance requirements are not the same station. That dangerous gas leakage detection in the rocket launch site, requires the mass spectrometer sensitivity as high as possible, but in the industrialized production field of semiconductor production and surface science, production environment could be as consistent as possible, which requires the mass spectrometer stability has better condition[2]. Mass spectrometer by the working principle of the restrictions, it is impossible to achieve the best performance of the various parameters, mass spectrometer ion source parameters should be adjusted according to actual needs. No doubt, among those influential factors, focusing voltage has great influence on the sensitivity of mass spectrometer. In this paper, the relationship between the sensitivity of QMS and the focusing voltage of ion source is studied by using the calibration device of mass spectrometer and using a single gas calibration method.

The focusing voltage of a common mass spectrometer ion source is adjustable. In this paper, QMG700 mass spectrometer (produced by Pfeiffer) was used as the research object, to study the relationship between the focusing voltage and the sensitivity of the QMS, and N₂ was used as the experimental gas. It is known that the sensitivity of the mass spectrometer could be obtained by the follow equation.

\[ S_i = \frac{I_i}{P_i} \]  (1)
Where, $S_i$ is the sensitivity of a mass spectrometer to some kind of gas $I$, A/Pa; $I_i$ is the ion current generated after ionization of gas $I$, A; $P_i$ is the partial pressure of gas $I$, Pa.

2. Establishment of Ion Source Physical Model

The mass spectrometer ion source is mainly composed of ionization chamber, filament and electronic collector, as shown in figure 1.

![Figure 1. Schematic diagram of ion source structure.](image)

1- Filament; 2- focusing electrode; 3- main slit; 4- grounding electrode; 5-slit $\beta$; 6-slit $\alpha$; 7- deflection electrode; 8- collimator magnet; 9- electronic collector; 10- ionization chamber; 11- repulsive electrode.

The electrons are emitted by the filament. These electrons are accelerated into the ionization chamber under the interaction between the accelerated voltage and the external magnetic field. In the ionization chamber, high-energy electrons collide with gas molecules, and the gas molecules are ionized. The ionized gas positive ions are led out by the ion optical system, then these ions are focused by the focusing voltage, and finally entered the mass spectrometer analyzer. The extra electrons that in the ionization chamber are collected by the electron collector [3]. Ion beam are focused by the focusing electrode of the mass spectrometer ion source. For specific geometric shapes of the electrode, the focusing performance of the focusing electrode at different electrode potentials is different. Due to the wide range of electrode potential, it is rather difficult to find the best focusing potential by experimental method. We need to simulate the electrostatic field of focusing voltage, so that it could be provide guidance for experimental adjustment and optimization of geometric size design.

3. Experimental system

This experiment is carried out on the calibration system of the mass spectrometer. The principle of the calibration system is shown in figure 2. The calibration system includes a calibration chamber, injection system, gas supply system, extraction system and quadrupole mass spectrometer which is selected QMG700 type quadrupole mass spectrometer with analog peak scan, multi-ion Detection and mixed gas concentration analysis and other functions.

The calibration method of the quadrupole mass spectrometer is as follows. After calibration system is pumped to the background, the gas is introduced into the regulator chamber 13 from the cylinder 7, and the gas pressure in the stable chamber is monitored by electrical resistance gauge 16 to ensure the gas entering the calibration chamber in the molecular flow state. Then the solenoid valve 16 is closed and the gas in the calibration chamber is adjusted by the micro-adjustment valve 11. When the gas in the calibration room is stable, the reading of the spinning rotor gauge 5 and the QMS are recorded. The values measured by the spinning rotor gauge and the QMS are compared, and the calibration of the mass spectrometer is completed. In the calibration process, the QMS is installed into the equator position of the calibration room 4. Spinning rotor gauge is fitted on the calibration chamber equator which has a 90 degree relationship with QMS to eliminate the effect of mass spectrometry.
1, 18, 20- mechanical pump; 2, 3, 19- molecular pump; 4- calibrated mass spectrometer; 5, 10-
spinning rotor gauge; 6- Ionization gauge; 7, 8, 14, 16- ball valve; 9-gap; 11- trimming valve; 12-
resistance vacuum gauge; 13- 5L stabilizer chamber; 15, 21, 22- solenoid valve; 17- gas cylinders.

Figure 2. The principle diagram of the calibration system for mass spectrometer.

4. Result analysis

In the working process of the QMS, the filament of the ion source is heated to produce electrons. These electrons get high energy under the action of accelerating voltage, then the gas molecules are ionized, and the ionized gas positive ions are led out by the ion optical system. These positive ions are focused by the focusing voltage, and finally led into the mass spectrometer analyzer. The extra electrons in the high-energy ionization chamber are collected by the electron collector. Therefore, adjusting the magnitude of the focusing voltage becomes an important factor to affect the sensitivity of the QMS. Due to the complex environment of the ion source, the gas positive ions are moving in the electromagnetic field. Based on the Maxwell equation, the focusing voltage is simulated and analyzed. The finite difference method is an important method to analyze the electric field problem. The fields to be solved are divided by grids, and finally the properties of the whole electromagnetic field are obtained. SIMION software is used to perform the simulation, and the simulation results are obtained.

In the SIMION software, the emission current and cathode voltage of the QMS ion source are set to a constant value. Only the voltage of the focusing voltage is changed, and the voltage is increased by 1V at a time. The effects on the sensitivity of the mass spectrometer are respectively tested. As shown in figure 3.

The results of SIMION software simulation show that the sensitivity of QMS is increasing rapidly with the increased focusing voltage. The sensitivity of the mass spectrometer reached a maximum value when the focusing voltage is 10V and 12V. Continue to increasing the focusing voltage, the sensitivity of the mass spectrometer will be smaller. Then we use the experiment to verify the results of the theoretical simulation.

The data acquisition and function control of QMG700 mass spectrometer can be completed by its own software. In the control software, the emission current, cathode voltage and focusing voltage of the QMS can be changed in a certain range. In this paper, the influence of the focusing voltage on the sensitivity of the mass spectrometer is tested. The test is conducted at a vacuum level of \(10^{-4}\) Pa. In order to obtain credible experimental results, the background vacuum of the system was required to below \(10^{-5}\) Pa [4]. The initial parameters of the quadrupole mass spectrometer use the default values of the built-in software. Before each calibration, the 30min is kept according to the state of calibration, so that the mass spectrometer could achieve a stable state.
After the chamber of calibration system is pumped to the background pressure which is $7.40 \times 10^{-6}$ Pa. The calibration gas is introduced into the calibration chamber. When the vacuum chamber is achieved dynamic balance, the partial pressure of the $N_2$ is $1.25 \times 10^{-4}$ Pa. The focusing voltage of the ion source is adjusted from 1 to 20V. Each adjustment interval is 1V. And then the sensitivity of $N_2$ is measured. The influence of the ion source focusing voltage on the sensitivity of the QMS is shown in figure 4.

Figure 3. The relationship between the focus voltage and the sensitivity.
Figure 4. Influence of focusing voltage on the sensitivity of mass spectrometer.

Through the analysis of figure 4, we can see that the experimental results and theoretical simulation results are consistent, that is, when the focusing voltage is small, the sensitivity of the mass spectrometer will increase with the focus voltage increasing. When the focus voltage reaches a certain Value, the sensitivity reaches the maximum. Increasing the focusing voltage continually, the sensitivity of the mass spectrometer will decrease as the focus voltage increasing.

5. Conclusions
The relationship between the focus voltage of the ion source and the sensitivity of the mass spectrometer shows a "peak type" distribution. When the focusing voltage varies from 9 to 13V, the sensitivity of the mass spectrometer reaches the maximum, while the sensitivity decreases rapidly on both sides of the peak. This phenomenon can be explained in two aspects. Firstly, when the focusing voltage is small, the ion beam is in the divergent state, and the ions are easily absorbed on the poles on both sides of the analyzer. The amount of ions entering the analyzer is reduced. Secondly, the ion energy coming from the ion source is relatively small, which leads to the ion velocity in the analyzer smaller and increases the retention time of ions in the analyzer. So that the unstable ions in the trajectory could be not passed through the analyzer, and the sensitivity of QMS is relatively small. With the increase of the focusing voltage, the ion beam slowly approaches the axis of the focusing pole. The number of ions entering the analyzer is increased greatly. The residence time of ions in the analyzer is reduced. More ions could be received by the receiving pole. So the sensitivity of QMS is increased. When the focusing voltage is too large, the ion beam deviates from the central axis of the focusing electrode, and more ions are applied to the plate. The passing rate of the ion flow decreases and the sensitivity is decreased.

The maximum sensitivity of the mass spectrometer is appeared at the focus voltage of 12V, which is 1.03% higher than the software default value and 146% higher than the focus voltage at 1V. It can be seen that when the focusing voltage of the ion source is in the default value, it could only play a negligible effect on the enhancement of the sensitivity of the mass spectrometer by adjusting the focusing voltage. But when the focus voltage is in the place far away from the peak, the adjustment of the focusing voltage could improve the sensitivity of the mass spectrometer. In addition, the focusing voltage could not become too large, otherwise the two ionization phenomena will be caused, which would cause the error of the mass spectrometer output.
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