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ScienceDirect
International Journal of Mass Spectrometry 270 (2008) 8–15
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Calibration of a frequency-scan quadrupole ion trap mass spectrometer for microparticle mass analysis

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Received 30 August 2007; received in revised form 16 October 2007; accepted 26 October 2007
Available online 9 November 2007

Abstract

Charge detection quadrupole ion trap (QIT) mass spectrometry (MS) is a promising technique for high-speed mass analysis of micron-sized particles such as biological cells and aerosols. In this technique, the trap can be conveniently operated in the mass-selective axial instability mode by scanning the frequency of the applied ac field under a low vacuum condition. However, because of the lack of proper mass standards in the m/z range of 10^9, a method of calibrating both the resolution and measurement accuracy of the mass spectrometer is required. Herein, we describe a calibration method which involves determination of the points of ejection (q_{eject}) of the individual particles to be analyzed and investigating how these q_{eject} points vary with the trap imperfection, the frequency-scan range, the scan speed, and the pressure of buffer gas. The results are compared with theoretical simulations based on the generalized nonlinear Mathieu equations. Using NIST polystyrene size standards as the test samples, we determined a mean ejection point of $q_{eject} = 0.952$ at the trap driving voltage amplitude of 1617 V, a He buffer gas pressure of 40 mTorr, and a frequency-scan rate of 70 Hz/s over the scan range of 450–100 Hz. The coefficient of variance of the measured q_{eject} points is 1.2%, suggesting that a resolution of ∼100 and a measurement accuracy of ∼1% can be achieved after careful calibration of the frequency-scan QIT mass spectrometer.
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Keywords: Quadrupole ion trap; Charge detection; Frequency scan; Microparticles

1. Introduction

Quadrupole ion trap (QIT) has been widely used as a mass analyzer since its invention by Paul et al. [1] and concurrently by Wuerker et al. [2] in the late 1950s. The device is robust, compact, and capable of providing high mass resolution when operating in the mass-selective axial instability mode [3–5]. Being an ion storage device, it has also been utilized as an electrodynamic balance for absolute mass determination of micron-sized particles such as aerosols [6] and synthetic polymers [7]. It is one of the most versatile mass analyzers available in the field.

When using the QIT as a microparticle balance, the frequency of the ac field applied to the ring and/or endcap electrodes is typically in the range of 1 kHz or less. Because of this low frequency, in order to achieve high mass measurement accuracy (better than 1%), only one particle is analyzed at a time over a time period of seconds up to minutes [8–13]. This long detection time, however, prevents the technique from routine and practical applications. A previous study [14,15] has shown that it is possible to integrate the mass-selective axial instability mode with the QIT for high-speed mass analysis of microparticles using light scattering as a detection method. A recent experiment [16] demonstrated that these particles can be detected by using an image charge detection plate which, additionally, provides a direct measure of the absolute number of the charges carried by the particles. This

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doi:10.1016/j.ijms.2007.10.012

newly developed technology has been successfully applied to measure the total dry masses and associated mass distributions of synthetic polymeric microparticles, cancer cells [16] and red blood cells [17].

In operating the QIT in the mass-selective axial instability mode, ramping up the ac voltage amplitude at a constant frequency is an effective approach, while ramping down the trap driving frequency at a constant voltage amplitude is the other [18]. The advantage of the latter is that the trap can be operated under mild vacuum conditions (pressure ~10 mTorr) without arcing between the ring and endcap electrodes. This is an important feature since it has been demonstrated [10–12,14,15] that gas damping is an effective means in reducing the total kinetic energy of the ionized microparticles produced by either electrospray ionization, matrix-assisted laser desorption/ionization, or laser-induced acoustic desorption (LIAD) for trapping. Evidence has also been found that the presence of buffer gas assists detection of the charged particles ejected from the QIT [16,17].

The feasibility of operating the QIT in the frequency-scan mode for analysis of high-mass biomolecules was first demonstrated by Schlunegger et al. [19]. The authors swept the trap driving frequency from 30 kHz to 10 kHz at a constant voltage amplitude of 200 V, and successfully obtained the mass spectra of singly charged IgG at $m/z \approx 1.5 \times 10^5$ with a mass resolution approaching 100. However, the difficulty in electronics hampered the operation of the frequency-scan QIT over a wider frequency range. The situation worsened when extending the study to larger biomolecules or bioparticles (such as viruses) since no suitable detector was available [7]. Very few work on the frequency-scan QIT-MS was reported since then, except those from our groups [16,17,20,21] and the Shimadzu group [22–25] working on digital ion traps.

This study was motivated by our recent development of charge detection QIT-MS for high-speed mass analysis of biological cells evaporated/ionized by LIAD [16,17]. In this analysis, in order for the cells to be effectively captured by the QIT and subsequently detected by the charge detection plate, the typical He buffer gas pressure used was in the range of 40 mTorr or higher. Because of this high pressure, it is crucial for the spectrometer to be operated in the frequency-scan mode so that the trap driving voltage can be maintained below the arcing threshold of the electrodes. However, it has been an open and important question how the buffer gas affects the ion ejection process at high pressures [26,27]. A method for calibrating the resolution and the measurement accuracy of the mass spectrometer, together with the sensitivity of the charge-sensitive detector, is thus required.

We have previously developed a method to calibrate the QIT operating in the voltage scan mode for mass analysis of microparticles [15]. Results of the calibration showed that the mass analyzer, a standard unstretched QIT, used in our experiment was imperfect. The trap imperfections may come from truncation of the hyperbolic electrodes, drilling of holes on the electrode assemblies, machining inaccuracy, as well as any possible misalignments between the ring and the endcap electrodes. Although there is a lack of mass standards in the m/z range of 10^9, both the resolution and measurement accuracy of this mass spectrometer can be properly characterized by a self-calibration method [15]. It involves high-precision measurement of the axial secular frequency (hence, its m/z) of a single particle inside the QIT, followed by monitoring the action of the ejection of this particle in real time to determine the point of ejection (q_{eject}). This work adopts the same method with the exception that the QIT is now operated in the frequency-scan mode. From a systematic measurement of more than 100 particles, a mean value of the measured q_{eject} and its distribution width were obtained. The results are compared closely with theoretical simulations based on the generalized Mathieu equations which take the gravity, the buffer gas damping effect, and the nonlinearity of the trapping field all into account.

2. Methods

2.1. Theory

The method of calibrating the QIT mass spectrometer consists of two parts. First, we characterize carefully the parameter β_z as a function of q_z near the boundary ($\beta_z = 1$) of the stability diagram of the QIT at $a_z = 0$ using a single trapped particle. For the QIT operating in the monopolar mode, either the ring electrode is grounded or the two endcap electrodes are grounded as employed herein, the two trap parameters are defined as [18]

$$\beta_z = \frac{2\omega_z}{\Omega} \tag{1}$$

and

$$q_z = \frac{4ZeV_{\text{ac}}}{mr_0^2\Omega^2}, \tag{2}$$

where ω_z is the axial secular frequency, Ω is the trap driving frequency, Z is the number of charge, e is the elementary charge, V_{ac} is the trap driving voltage amplitude (i.e., zero-to-peak voltage), m is the ionic mass and r_0 is the radius of the ring electrode. For an ideal QIT, $q_{\text{eject}} = 0.908$ at $\beta_z = 1$; however, this point may shift due to the trap imperfections [28]. We determine the value of β_z directly from a measurement of ω_z for a single charged particle oscillating inside the trap according to Eq. (1) and calculate the mass-to-charge ratio of this particle at $\beta_z \leq 0.2$, where the pseudo-potential approximation [18,29]

$$\beta_z = \frac{q_z}{\sqrt{2}} \tag{3}$$

applies as [2,29]

$$\frac{m}{Ze} = \frac{\sqrt{2}V_{\text{ac}}}{r_0^2\Omega\omega_z}. \tag{4}$$

With this m/Ze the q_z value at given r_0, Ω and V_{ac} can be calculated from Eq. (2) accordingly. A plot of β_z versus q_z can be therefore derived from repeated measurements of ω_z at various Ω over the range of $\beta_z = 0$–1 for the same particle (i.e., with the same m/Ze). Fig. 1 shows a typical result of such measurements.

Second, we monitor the action of the particle ejection in real time when the trap driving frequency is ramped down. From the measured ejection frequency (Ω_{eject}), the q_{eject} value of

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