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Quantitative mass spectrometry by orthogonal projection method with periodic signal of electrostatic ion beam trap

Qi Sun[a,*], Changxin Gu[a], Li Ding[b]

[a] Department of Materials Science, Fudan University, 220 Handan Rd., Shanghai, 200433, People's Republic of China
[b] Shimadzu Research Laboratory Shanghai Co. Ltd., 108 Second Kayuan Rd, Shanghai 201201, People's Republic of China

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ABSTRACT

In this paper, orthogonal projection method (OPM) is introduced which could perform quantitative mass spectrometry with signal of electrostatic ion beam trap (EIBT). In order to acquire periodic current signal, a model of EIBT with cylindrical-detector is set up to simulate ions oscillatory motion. Where after, OPM is introduced and applied for quantitative mass spectrometry. It shows that quantitative MS with high precision could be obtained by OPM with sampling time short as 200 μs. Comparing with FFT, the mass spectrometry performed by OPM is characterized by higher precision and much shortened sampling time. OPM mass spectrometry is influenced by several factors, including the length of sampling time, mass detecting interval δM, tested ion mass and its location in the mass detecting interval, which are discussed systematically. The OPM results show that, the effective sampling time for quantitative MS should be prolonged when the tested ion mass is increased or the mass detecting interval is decreased. The shortest effective sampling time T_{90S} and the longest effective sampling time T_{90L} are all proportional to $M^{3/2}/\delta M$, and the relation of which is specified by linear regression.

1. Introduction

EIBT (electrostatic ion beam trap) has been invented and developed during the last decade, which stores and manipulates ions with only electrostatic fields [1–4]. When a group of ions is injected into EIBT, they would be trapped and oscillate between the two parallel sets of electrode mirrors with applied voltages, which working principle is similar to that of an optical resonator, and accordingly endows EIBT with another name of ion-trap resonator [5–7]. It has been demonstrated that EIBT is a competent instrument to perform various experiments both in physics and in chemistry, such as lifetime measurement of metastable state atomic, molecular and negative ions [8–11], electron-impact experiments [12,13], beam dynamics and mass spectrometry [14,15].

As the ions are constrained by the electrode mirrors, they oscillate back and forth and induce periodic current signal on the detector which is mounted in the middle of EIBT [16]. The periodicity of the signal characterizes the mass of the oscillating ions, and with frequency analysis of which, the mass spectrometry can be performed. Consequently, EIBT could be used as time-of-flight mass spectrometry, in which the flight path of the ions is multiple folded by electrode mirrors, and thus high resolution of mass analysis is expected.

FFT (fast Fourier transform) is conventional method to analyse periodic signal and acquire frequency spectrum, and the EIBT mass spectrometry acquired are all based on this method [14,15]. However, the frequency spectrum of FFT is quite complex, in addition to the fundamental harmonic, more than ten higher order harmonics exist with prominent intensity, which encumbers mass spectrometry, especially different kinds of ions compounded together. In addition, more accurate frequency spectrum means longer sampling time, and which should be at least several hundreds milliseconds to perform MS. In the case of prolonged sampling time, the dispersion effect of the ions should be taken into consideration, which would tamper the periodicity of the oscillating ions and do harm to mass spectrometry. Moreover, it is impossible to indicate the quantity of the detected ions through frequency analysis of FFT.

In this paper, orthogonal projection method (OPM) is introduced which could perform quantitative mass spectrometry with high precision and with much shortened sampling time. Current signals of ions with certain mass number are adopted as basis vectors in OPM, which is consistent with particular EIBT setup. The current signal of tested ions could be orthogonal projected to these basis vectors, and the coefficients of projection could not only specify the mass number of the tested ions, but also indicate the amount of those ions. As shown in this paper, sampling time of OPM is much shortened comparing with FFT, e.g., for ions with mass number ~100, quantitative MS above 90% accuracy can be acquired with sampling time short as several

* Corresponding author. Tel.: +86 21 65643649; fax: +86 21 65643647.
E-mail address: sqhit@fudan.edu.cn (Q. Sun).

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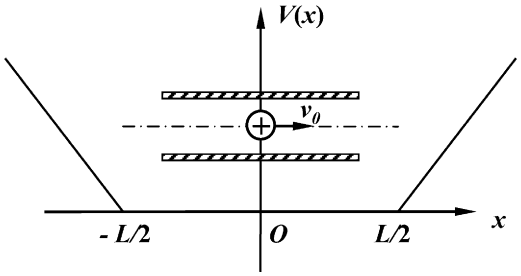

Fig. 1. Schematic figure of linear trapping potential field of EIBT with single-cylindrical detector mounted in the middle.

hundreds microseconds, which is impossible to be performed by FFT.

The model that generates EIBT periodic signal is described in Section 2, and orthogonal projection method is introduced in Section 3. Results and discussion are presented in Section 4, in which several factors that influence the result of OPM mass spectrometry are discussed, and conclusions are given in Section 5.

2. Numerical modeling

In order to simulate the motion of the ions and acquire the periodic signal, a model of EIBT is established. According to the experimental setup [14], the whole length of EIBT is set to be 400 mm, and the length of central field-free region is set to be 200 mm. A linear trapping potential field that constrains ions motion is set up in EIBT as shown in Fig. 1, and the electric field is formulated as a function of $\boldsymbol{x}$.

$$E(x) = \begin{cases} k & x < -L/2 \\ 0 & |x| < L/2 \\ -k & x > L/2 \end{cases} \quad (1)$$

where L corresponds to the length of central field-free region, and the gradient k of potential characterizes the electric field in the region of electrostatic mirrors. In the central field-free region of EIBT, a single-cylinder detector is used to detect the induced current, and the details of the modeling of induced current have been discussed in the former publication [16,17]. The length and radius of the cylindrical detector are selected to be 10 mm and 5 mm respectively.

Moving ion with mass m is assumed to carry single charge e, with its initial position being set in the center of the potential field as shown in Fig. 1. The initial velocity v_0 is determined by the initial energy E_0 according to Eq. (2)

$$v_0 = \sqrt{\frac{2E_0}{m}} \quad (2)$$

In the simulation, E_0 is set to be 4.2 keV and k is set to be 200 kV/m, and thus the oscillation period of argon ions in such an modeling setup is about 6 μs.

In order to simplify the problem, following assumptions are introduced:

(1) Moving ions are assumed to have the same energy with neglecting their energy dispersion.
(2) The ions move along the axis of the cylindrical detector, and their energy remains unchanged when passing through the detector. This assumption is legitimate as discussed previously [16,17].
(3) As sampling time in the simulation is restricted in 10 ms, Coulomb reaction between positive charged ions is not considered in the simulation.

According to the assumptions above, the only force seen by the moving ions is the electric force applied by the electrodes. The ions motion equation is

$$E(x)e = m\frac{d^2x}{dt^2} \quad (3)$$

Leap-frog differential scheme is applied to acquire ions velocity and ions position at each time step. With the simulation results of the ions motion, the periodic image current signal induced on the detector could be acquired, which corresponds to the ions oscillate with certain frequency according to their mass [14,15].

According to the idealized simulation setup, the period T_0 of the ion with mass m and charge e is

$$T_0 = \left(\frac{2L}{\sqrt{2E_0}} + \frac{4\sqrt{2E_0}}{ke}\right)\sqrt{m} \quad (4)$$

With introducing specified E_0, k, L and relative constants, the period of ions motion in this model EIBT is

$$T_0 = 0.630168\sqrt{M}\,(\mu s) \quad (5)$$

Where M is the mass number of the moving ions. As single-cylindrical detector is adopted in the simulation to detect image current signal, the period of the signal is one half of that of the ions motion

$$T_s = \frac{T_0}{2} = 0.315084\sqrt{M}\,(\mu s) \quad (6)$$

And the frequency of the detected signal is

$$f_s = \frac{3.173757}{\sqrt{M(\text{amu})}}\,(\text{MHz}) \quad (7)$$

and the mass number M is related to the signal frequency according to

$$M = \frac{10.07273}{f_s^2} \quad (8)$$

As the period of signal acquired in EIBT is proportional to the square root of the ions mass number, and with determining the frequency of the signal by frequency analysis (e.g., FFT), the mass number of the ions can be specified by Eq. (8).

In Fourier transform, the length of sampling time T in time domain determines Δf, the indeterminacy in frequency domain, which satisfies the relation of $\Delta f = 1/T$. And the relation between the indeterminacy of mass number and that of frequency is derived from Eqs. (7) and (8)

$$\Delta M = 0.630168M^{3/2}\Delta f \quad (9)$$

Accordingly, the longer sample time implies the higher precision of frequency analysis. In our simulation, the length of longest sampling time is selected to be 10 ms, thus $\Delta f = 0.0001$ MHz, and according to Eq. (9), the indeterminacy of mass number is

$$\Delta M = 6.30168 \times 10^{-5}M^{3/2} \quad (10)$$

From the equation it is clearly shown that, ΔM increases with increasing the mass number with the order of 1.5, which means the indeterminacy of mass increases remarkably with increasing the mass of the detected ions.

Fig. 2(a) shows the periodic image current signal induced by the ions of mass number 100.01 with 10 ms sampling time and 10 ns sampling interval, and the ions' number is selected to be unit amount. Fig. 2(b) is the corresponding frequency spectrum performed by FFT. As shown in the figure, the signal waveform deviates evidently from the harmonic waves, which are used as the basis function in FT, and thus brings complexity to FFT frequency spectrum. In addition to the fundamental harmonic which corresponds