Available online at www.sciencedirect.com

ScienceDirect

International Journal of Mass Spectrometry 264 (2007) 181–183

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Coupling an atmospheric pressure ion source to a mass spectrometer: A new method

Z.Z. Latypov *, G.K. Golikov

Institute for Analytical Instrumentation RAS, Rizhsky 26, 190103 St. Petersburg, Russia

Received 1 February 2007; received in revised form 2 April 2007; accepted 15 April 2007
Available online 25 April 2007

Abstract

In this work a new method of monochromatization and formation of the ion beam produced by an ion source operating at high gas pressure and other types of sources producing the ion flux with a wide energy range distribution is proposed. The method is based on converting the ion energy spectrum by the electric field pulse shock on ions in high vacuum and the subsequent passing of the beam through the focusing electrostatic lenses. Analytical expressions for estimating the time and space characteristics of the ion energy dissipation are derived. The proposed method is radically different from the those based on the dissipation ion energy in the collision cells.

Keywords: Ion source converter; Energy monochromater; Function of energy distribution

1. Introduction

The development of ion beam monochromatization methods is still relevant since various types of ion sources producing ions with a wide energy dispersion (for example MULDI source, ESI source) are used in mass spectrometry. The monochromatization and formation of an ion beam produced by the ion source working at high background gas pressure (ESI source, ICP source and others) is important for the efficient coupling between the ion source and the high vacuum part of mass analyzers. Ions undergoing expansions in vacuum acquire a high velocity and spatial dispersions. The formation of an ion beam in the interface plays a dominant role in improving both the ion transmittance and the quality of mass measurements by normalizing energy.

In the works [1–3] methods of ion transport from ion sources to high-vacuum part of a mass analyzer have been proposed. Theoretical and experimental investigations of these methods have been accomplished. These methods differ basically in the construction of respective devices. They are based on using radiofrequency (rf) field constraining the ions close to the axis, while the necessary dissipative forces are provided by collisions with the atoms of gas which is at an intermediate pressure in volume of RF system. One of these methods is presented in detail in theoretical work [3].

In Ref. [3] the results from developing a collisional focusing ion guide (CFIG) for coupling atmospheric pressure ion source to a mass spectrometer are presented. The CFIG operation is based on the focusing action of the effective RF potential which creates a potential well along the axis of a multipole system. The energy of ions coming from the ion source through an input orifice is dissipated in collisions with molecules of a buffer gas with pressure in the range $10^{-2} < p < 1$ Torr. CGIG is provided with an additional systems of differential pumping out The ions are transported to the exit orifice by the gas flow or additional dc potential.

The dynamics of an ion moving in a medium with temperature T estimated from the Fokker–Plank equation is described by the following expression for function $W(u, t)$ of probability distribution in the velocity space u:

$$W(u,t) = [\pi V_g^2(t)]^{-3/2} \exp\left(-\frac{|u - u_0 \exp(-t/\tau)|^2}{V_g^2(t)}\right),$$

$$V_g^2 = \frac{2kT}{M}\left(1 - \exp\left(\frac{-2t}{\tau}\right)\right). \quad (1)$$

---

* Corresponding author. Tel.: +7 812251 8159; fax: +7 812251 7038.
E-mail addresses: Latypov@ianin.spb.su, Zeidel@yandex.ru (Z.Z. Latypov).

1387-3806/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2007.04.010

Here $W(u,t)$ is the Gaussian distribution whose width $V_g^2(t)$ approaches $2kT/M$ exponentially, u_0 is initial velocity:

$$\tau = \frac{3(m+M)}{4mn\sigma v} \tag{2}$$

is a characteristic time for energy dissipation of the ion while it is moving in a buffer gas, M is the ion mass, m the gas atom mass, n the density of the buffer gas, v the velocity of the gas atoms and σ the cross section for collisions of ions with atoms. The limit of (1) for $t \gg \tau$ results in Maxwellian distribution $\sim\exp(-Mu^2/2kT)$. The mean squared velocity is $u^2 \rightarrow 3kT/M$, therefore the energy of the ion approaches thermal equilibrium with the medium. The energy dissipation path may be estimated as $L_{kT} - u_0\tau$. However the length of the ion guide should be sufficient for cooling ions of different initial energy. Thus $L_G > L_{kT}$. In Ref. [3] some examples are numerically estimated: In case $M = 1000$ u, $m = 40$ u, $\sigma \approx 10^{-15}$ s m^2, $p \approx 10^{-1}$ Torr, $Mu_0^2/2 \approx 10$ eV, the frequency of collisions is $f \approx 3.7 \times 10^5$ s^{-1}, the dissipation time $\tau \approx 5 \times 10^{-5}$ s, and the dissipation path $L_{kT} > 1$ s m.

The considered method was used [4,5] for coupling MALDI source to mass spectrometers.

The major disadvantages of these methods is the reducing of the ion flux intensity from the source due to the charge exchange and other inelastic processes when ions collide with buffer gas atoms.

2. Monochromatization of ion beam energy by means of shocking ions with the electric field pulses

We propose a new alternative method of modifying the ions energy distribution function in the phase space. The method is based on a radically new mechanism of action on ion motion parameters by a sequence of short electric pulses (electric shocks) [6,7]. Here we use our method for monochromatizing the ion beam. However, it can also be applied in other areas where it is necessary to establish the desired statistic for the obtained ions.

In our works [6,7] the general conception of transforming the mass spectrum into the energy spectrum of particle flux was developed, which enables us to came up with a new method of dynamic mass spectrometry. Here we apply our ideology to beams monochromatization.

In the present study we suggest a method where the monochromatization of the ion flux is performed in a high vacuum. Thereafter the flux is passed through the focusing electrostatic lenses. The essence of the method (theory) is as follows. A particle with mass M moving with kinetic energy E_0 acquires additional energy ΔE provided it is acted upon by force in the direction of the motion within a short period of time Δt. Thus the final kinetic energy is

$$E = E_0 + \Delta E = E_0 + (F\Delta t)\sqrt{2E_0/M} + (F\Delta t)^2/2M, \tag{3}$$

where $(F\Delta t) = \int_0^{\Delta t} F(t)\mathrm{d}t$ is the value of particle momentum change, and ΔE is the energy change. Since we consider here the pulse electric field action on ions, the active force is $F(t) = qV(t)/L$, where q is the charge of ions, $V(t)$ the potential of the electric pulse, and L is the linear size of the conversion region. If the active force is directed opposite to the initial velocity of a particle, the value of the energy change ΔE in (3) is negative.

The ion beam produced by the ion source with the energy E_0 has a wide range of energy distribution. The monochromatization of the beam and the minimization of energy dispersion can be achieved by multiple electric pulses action on the ions during their flight time in the conversion region and by changing the value ΔE_i according to the Maxwellian distribution function:

$$f_{\mathrm{Max}}(\Delta E_i) = \frac{2}{\sqrt{\pi}}(kT)^{-3/2}\,\mathrm{e}^{-\Delta E_i/kT}\sqrt{\Delta E_i}$$

Therefore what is required is the repeated action of electric pulses on particles, and values $(F\Delta t)$ should obey the Maxwellian function.

It is obvious from Eq. (3) that the energy change depends on the ion mass. Since monoenergetic flux of ions of various mass is a necessary condition in mass spectrometry, the dependence of ΔE on M is eliminated by accelerating ions with the following deceleration in the same conditions. In this case the final kinetic energy of ion is equal to

$$\begin{aligned} E = E_0 &+ \sum_{i=1}^{n}(F\Delta t)_i\sqrt{\frac{2E_i}{M}} + \sum_{i=1}^{n}\frac{(F\Delta t)_i^2}{2M} \\ &- \sum_{i=n+1}^{2n}(F\Delta t)_i\sqrt{\frac{2E_i}{M}} - \sum_{i=n+1}^{2n}\frac{(F\Delta t)_i^2}{2M}, \end{aligned} \tag{4}$$

where n is the number of pulse action.

Particular emphasis should be placed on the principal physical difference of the proposed ions-electric pulses interaction mechanism from the ions-atoms interactions in collision cells with the buffer gas. The pulsed electric field in this case should be considered as the transparent equivalent of a buffer gas. In the interaction process of ion with electric pulse the value and direction of the ion momentum are changed as in the case of ion - atom collision. However, the transformation of the ion velocity vector direction is much lower than in case of elastic ion-atom collision. Therefore it can be considered as an advantage of a ion-electric pulse interaction.

It is required to find the value of relaxation time τ determining the efficiency of the energy dissipation in conversion process, which enables the estimation of the energy dissipation path L_{kT}. The shock interaction of ions with electric pulses can be considered as elastic frontal collisions of ions with some particles resulting in the changes of ions energies ΔE and momentum $(F\Delta t)$. Taking into account the conservation laws of energy and momentum within the adopted model, we find values of effective mass $m = F\Delta t)^2/2\Delta E$ and velocity $v = 2\Delta E/(F\Delta t)$ for imaginary particle. As a result, we derived the analytical expressions for characteristics time and energy dissipation path of ions taking

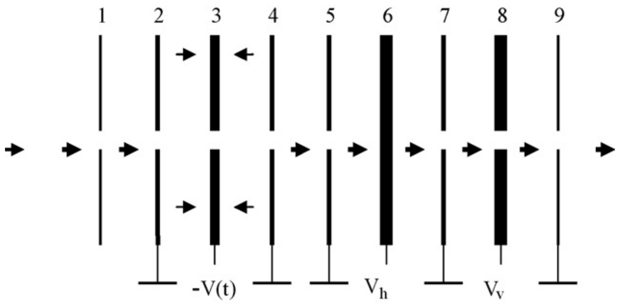

Fig. 1. The schematic arrangement of ion flux monochromator: (1) is the exit orifice of ion source, (2) is the input orifice of monochromator, (3) is the electrode with applied voltage $V(t)$, (4) is the electrode for passing ion flux through electrostatic lenses of the horizontal focusing (with potential *Vh*) and of the vertical one (with potential $V_{\rm v}$) and (9) is the input slit of a mass spectrometer.

into account (2) and (4):

$$\tau_{\rm el} = \frac{3u_0}{4f}\sum_{i=1}^{n}\left[\frac{(F\Delta t)_i}{2\Delta E_i} + \frac{M}{(F\Delta t)_i}\right] - \frac{3u_0}{4f}\sum_{i=n+1}^{2n}\left[\frac{(F\Delta t)_i}{2\Delta E_i} + \frac{M}{(F\Delta t)_i}\right] \quad \text{and} \quad L_{\rm el} = \tau_{\rm el} u_0$$

The following numerical examples serves to illustrate the proposed method. For the Eqs. (3) and (4) to be fulfilled, the voltage pulse duration Δt must be shorter than the time of flight $t_{\rm L} = L\sqrt{M/2\left(E_0 + \sum_{i=1}^{n}\Delta E_i\right)}$ in the space of spectra conversion. The Maxwellian distribution of the pulse amplitudes in this case is a consequence of voltage pulses with duration Δt frequency f and period T when the amplitude changes according to the function $f_{\rm Max}(V(t))$. If this function includes $n_{\rm M} = 200$ pulses with period $T = 5\Delta t$, the period of repeated function $f_{\rm Max}(V(t))$ equals $T_{\rm M} = t_{\rm L}/n_{\rm M}T$. The numerical estimation based on the described model shows that at $M - 1000$ a.u., $E_0 \sim 50$ eV, $\Delta t \approx 10^{-7}$ s, $V(t) - 200$ V and $f - 20$ MHz the dissipation time and path are $\tau_{\rm el} - 4 \times 10^{-5}$ s and $L_{\rm el} - 6$ s m, respectively. These characteristics can be considerably improved provided the values of $V(t)$ and f are increased.

The ion spectra are converted in the ion source converter when the ion flux is passed trough the space between the electrodes of the condensers. The electric potential difference is applied to the electrodes as a consequence of voltage pulses $V(t)$. Fig. 1 shows the schematic arrangement of the ion flux monochromator: (1) is the exit orifice of the ion source, (2) is the input orifice of the monochromator, (3) is the electrode with applied voltage $V(t)$, (4) is the electrode for passing the ion flux through electrostatic lenses of the horizontal (with potential *Vh*) and vertical (with potential $V_{\rm v}$) focusing and (9) is the input slit of a mass spectrometer. The space between electrodes 2 and 3 is the accelerating space, the space between 3 and 4 is the decelerating one. These spaces have equal linear sizes L. "Thermolized" ions can be accelerated, if necessary, in front of electrostatic lenses.

3. Conclusion

Special emphasis should be made on the characteristics of the physical mechanism of the ion flux interaction with the "transparent electromagnetic gas" with controllable statistics. The collision with the electromagnetic pulse is similar to that of the particles without singularities, which enables the harmonic agreement of the ion source with the mass spectrometer.

In this work a method of monochromatization and formation of ions beam produced by an ion source at high gas pressure and others types of sources producing ion flux with a wide range of energy distribution is proposed The method is based on the electric shock mechanism of the ion energy conversion in high vacuum and the subsequent passing of the beam through the focusing electrostatic lenses. Analytical expressions to estimate time and space characteristics of the ion energy dissipation are derived. The numerical estimations show that these characteristics are superior to the identical ones of CFIG.

The proposed method has the following advantages over the methods described in literature: (a) the proposed method will be indispensable for coupling ion sources of *any* kind to a mass spectrometer; (b) it allows to obtain ion beams with higher intensity since there are no losses of ions due to the charge exchange and to other inelastic collisions; (c) as compared to the CFIG, the new method is technically much simpler to realize; (d) no additional differential pumping out systems are needed.

References

[1] K. Standing, B. Thomson, M. Wilm, Rapid Commun. Mass Spectrom. 11 (1997) 1015.
[2] A.F. Dodonov, V.I. Kozlovski, I.V. Soulemenkov, V.L. Laboda, K.G. Standing, et al., Eur. J. Mass Spectrom. 6 (6) (2000) 481.
[3] A.V. Tolmachev, I.V. Chernushevich, A.F. Dodonov, K.G. Standing, Nucl. Instrum. Methods Phys. Res. B 124 (1997) 112.
[4] A.N. Krutchinsky, A.V. Laboda, V.L. Spicer, R. Dwoschak, W. Ens, K.G. Standing, Rapid Commun. Mass Spectrom. 12 (1998) 508.
[5] A.V. Laboda, Proceedings of the 53th ASMS Conference, 2005.
[6] Z.Z. Latypov, L.N. Gall, G.K. Golikov, Int. J. Mass Spectrom. 202 (2000) 139.
[7] L.N. Gall, G.K. Golikov, Z.Z. Latypov, N.A. Timchenko, Nucl. Instrum. Methods A 423 (1999) 461.