Linear Time-of-Flight Mass Spectrometers: Postsource Pulse Focusing Conditions and Mass Scale

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The condition to cancel aberrations that result from initial ion velocities and length of ionization process by postsource pulse focusing in linear time-of-flight mass spectrometers is derived. The ion arrival time distribution as a function of ion mass is given, which permits mass scale calibration. Simple formulas allow calculation of the voltage needed for postsource pulse focusing and the limits of the mass range where the focusing action is felt. The theory is illustrated for a specific instrument case. (*J Am Soc Mass Spectrom* 1995, 6, 889–891)

To improve the resolution of linear time-of-flight mass spectrometers (TOFMS) variable electric fields have been applied to ion drift regions between the ion source and detector. Velocity compaction [1], postsource pulse focusing (PSPF) [2], and dynamic field focusing [3] are all such procedures that have been presented in literature. PSPF has been modeled by computer [2], experimentally demonstrated for gas-phase ionization [4], and mass spectra with resolutions of 2900 have been recorded for laser desorbed ions produced in the TOFMS instrument described in ref 5.

The aim of the present short communication is to derive the focusing condition and mass scale as well as to give simple formulas to calculate the instrumental parameters needed for implementation of PSPF.

The flight times over various ion acceleration regions were calculated by using the formulas of ref 6, and are rewritten in terms of velocities:

$$t = (m/(zeF))(v_{out} - v_{in}) \quad (1)$$

$$v_{out} = (v_{in}^2 + 2zeFL/m)^{1/2} \quad (2)$$

where t is the time spent by the ion traveling across a region of length L while accelerated by an electric field of strength F . The ion of mass m and z elementary charges e enters and leaves the region with longitudinal velocity v_{in} and v_{out} , respectively. Let us consider an ion created at a distance s_0 from the ion source reference plane P (Figure 1) that has initial longitudinal velocity v_0 directed toward the detector at a moment t_0 after the beginning of the ionization event, taken as the time origin. The source reference plane is

normal to the ion packet movement direction, in the middle of the ionization region. The reference ion of mass m , created at the time origin and starting from rest, from the source reference plane will be detected t_{of} later. By using (1) and (2) twice we find the first order approximation for the time t_2 needed by this ion to travel through the source and secondary acceleration regions, where constant fields were applied:

$$t_2 = (D_s/v_s)[1 + s_0k/(2D_1\sigma^2)] - mv_0/(zeF_1) \quad (3)$$

while the ion longitudinal velocity is there:

$$v_2 = v_s[1 + s_0/(2\sigma^2D_1)] \quad (4)$$

The symbols are defined in Table 1 and by the relations

$$D_s = 2\sigma[D_1 + D_2/(1 + \sigma)]$$

$$\sigma^2 = U_s/(eF_1D_1)$$

$$v_s = (2U_s/m)^{1/2}$$

$$k = \sigma^2[D_1(1 + \sigma) - D_2/\sigma]/[D_1(1 + \sigma) + D_2]$$

The PSPF field is established between the planes F and G , at a moment T from the time origin. Because the ion was allowed to drift freely along $v_2(T - t_0 - t_2)$, it needs time t_3 to travel the remaining D_3 after the PSPF field is applied:

$$t_3 = m(v_3 - v_2)/(zeF_3) \quad (5)$$

The ion velocity at the plane G is increased to v_3 :

$$v_3 = \{v_2^2 + (2zeF_3/m)[D_3 - v_2(T - t_0 - t_2)]\}^{1/2} \quad (6)$$

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Figure 1. Linear time-of-flight mass spectrometer with post-source focusing grid: basic geometric parameters.

Table 1. Definitions of symbols used in text

Symbol	Physical meaning ^a
D_1	Source region length
D_2	Secondary acceleration region length
D_3	PSPF region length
D_4	PSPF grid-detector distance
s_0	Initial ion distance to the reference plane
F_1	Source region field strength
F_2	Secondary acceleration region field strength
F_3	PSPF region field strength
v_s	Reference ion velocity at source exit
v_f	Reference ion velocity before detection
v_0	Initial ion velocity
U_s	Reference ion energy at source exit
U_f	Reference ion energy before detection
t_{f0}	Reference ion total flight time
t_0	Instant when ion created

^aThe reference ion was created at the source reference plane P , at rest, when the ionization process started (time origin).

The ion is detected at t_f from the time origin:

$$t_f = T + t_3 + t_4 \quad (7)$$

with $t_4 = D_4/v_3$ time spent in flight over the last field-free space. A complete first order series development in the small quantities t_0 , v_0/v_s and s_0/D_1 gives:

$$t_f = t_{f0} + \delta t_1 + \delta t_2 + \delta t_3 \quad (8)$$

where δt_1 , δt_2 , and δt_3 are flight time deviations for an ion with initial parameters s_0 , t_0 , and v_0 , respectively, related to the reference ion:

$$t_{f0} = T + (2m)^{1/2} \left[\frac{U_f^{1/2} - U_s^{1/2}}{zeF_3} + \frac{D_4}{2U_f^{1/2}} \right] \quad (9)$$

$$\delta t_1 = \left\{ \left[\frac{1 - zeF_3 D_4}{mv_f^2} \right] \left[\frac{mv_s^2}{zeF_3} + D_3(1 + k) - v_s T \right] / v_f - \frac{mv_s}{zeF_3} \right\} \frac{s_0}{2D_1\sigma^2} \quad (10)$$

$$\delta t_2 = \left(\frac{v_s}{v_f} \right) \left[1 - \frac{zeF_3 D_4}{mv_f^2} \right] t_0 \quad (11)$$

$$\delta t_3 = - \frac{mv_s v_0}{v_f zeF_1} \left[1 - \frac{zeF_3 D_4}{mv_f^2} \right] \quad (12)$$

The final energy and velocity result from the relation

$$U_f = mv_f^2/2 = U_s + zeF_3 [D_3 + D_s - T(2U_s/m)^{1/2}]$$

Simultaneous arrival at the detector of the ions created at different moments and that possess different initial velocities is possible by canceling simultaneously δt_2 and δt_3 , which happens when

$$mv_f^2 = zeF_3 D_4 \quad (13)$$

This statement, which was established for ions that originate from solid surfaces with initial velocity components directed only toward the detector, is also valid for ions produced from gaseous samples. For ions with initial velocities directed against the electric field sense, the turnaround time must be added simply by changing the sign of v_0 in (12). If the remaining term in s_0 is unimportant for ions from surfaces, the violation of "space focusing" may be troublesome for ions produced from gas molecules. To optimize the instrument in such a case the three contributions in v_0 , s_0 , and t_0 to the packet final size should be balanced [6].

Only ions inside the section D_3 at the time the field F_3 is established will be focused. The ions that just entered into the D_3 section are focused best when the PSPF field is established, rather than near its detector side end. Therefore, the mass range of the ions that undergo PSPF will be confined to the interval:

$$m_{\min} = 2U_s T^2 / (D_s + D_3)^2 \quad (14)$$

$$m_{\max} = 2U_s T^2 / D_s^2 \quad (15)$$

In the last expression the small correction due to the packet length was neglected.

The velocity-time focusing condition (13) is satisfied for a mass close to $m_{\max}$ because these ions typically exhibit the poorest resolution. Then $U_f \approx U_s + zeF_3 D_3$ and the voltage V_{appl} to be applied across the PSPF region can be estimated to be

$$V_{\text{appl}} = V_{\text{ac}} / (0.5D_4/D_3 - 1) \quad (16)$$

where V_{ac} is the overall ion source accelerating voltage.

The instrument resolution R may be estimated from first order terms accounted for in the packet length with the formula

$$R = t_{f0} / [2(|\delta t_1| + |\delta t_2| + n|\delta t_3| + \delta t_e)] \quad (17)$$

Figure 2. Resolving power over the mass range where PSPF acts. The resolving power for the frontier mass (240.85 u) was taken as unity; the components related to s_0 and v_0 are neglected.

Here δt_c is the detector time resolution. If the initial ion distributions are rectangular of widths s_0 in space, t_0 in time, and v_0 in velocities, eq 17 gives the TOFMS resolution at the base of the peak. For ions that come from a surface $n = 1$, whereas for gas samples n should be substituted by 2 to account for turnaround time. For realistic initial velocity distributions, v_0 is to be taken as the velocity of the fastest ions with nonnegligible population.

The flight time of the reference ion t_{f0} as a function of the mass represents the law for mass scale calibration. It is expressed through constants to be determined from known flight times of at least five ion masses:

$$t_{f0} = a_0 + a_1 m^{1/2} \left[(1 - a_2/m^{1/2})^{1/2} - a_3 + a_4/(1 - a_2/m^{1/2})^{1/2} \right] \quad (18)$$

For the specific case of the instrument of ref 5, if ions of $m_{\max}/z = 1050$ u with $U_k = 7$ keV are admitted in the PSPF region, for $\sigma^2 = 14$, the foregoing formulas give $V_{\text{appl}} = 732.98$ V, $T = 2.3064$ μs , $m_{\min}/z = 241$ u (more precisely 240.85 u). If the focusing condition eq 13 is satisfied for ions of $m/z = 1048$ u, for $V_{\text{appl}} = 732.92$ V and δt_c is neglected, the obtained resolution of 2900 would be limited to this value only due to the first order term in s_0 . Thus the total thick-

ness of the ionization region—surface and field nonuniformities included—results from eq 17: $s_0 = 5.5 \times 10^{-2}$ mm.

The capability of the PSPF method is illustrated by the mass dependence of the resolving power when the t_0 term dominates. The curve of Figure 2 was traced by taking the resolving power for the smallest still-focused mass $m_{\min}$ as unity. The resolution is increased by a factor of 2 at $m/z = 419$ u and by a factor of 4 at $m/z = 618$ u.

The derived formulas are useful for implementation of PSPF. They allow calculation of the applied voltage, the time delay to focus a selected mass (simpler than those of ref 4), the mass scale, and the theoretical resolution over the focused mass range for a given set of ion formation conditions.

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