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Dynamical Behavior of Ions in a Radio Frequency Spark Ion Source

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The dynamical behavior of ions in a radio frequency spark ion source as a consequence of residual voltage oscillations during spark breakdown has been studied. Calculation of ion trajectories in the spark box showed that the transmission of ions is dependent on the phase angle between the residual potential oscillation and the departure of an ion. The interval of transmitting phase angles decreases toward lower masses, representing a mass discrimination.

INTRODUCTION

Radio frequency (rf) spark discharge has found wide applications in emission spectrometry and mass spectrometry, where it is used as an excitation and ionization source, respectively. Spark source mass spectrometry (SSMS) in particular has proven in the past few decades to be one of the most sensitive techniques for the "panoramic" analysis of high-purity materials, but the sometimes poor reproducibility (ca. 20%) and extended analysis time remain major drawbacks. The phenomena occurring during a spark breakdown that lead to the detected ions have been investigated thoroughly (*1–3*) but did not bring about a significant improvement on the part of the reproducibility.

As a result of the availability of commercial equipment, glow discharge mass spectrometry (GDMS) is becoming the main competitor of spark source mass spectrometry. In the glow discharge ion source a stationary discharge plasma gives rise to a better reproducibility and a comparable or even higher sensitivity. Still it seemed worthwile to revisit the problem of ion extraction in an rf spark ion source to see whether additional information can lead to an improvement of the technique in terms of speed, reproducibility, and accuracy.

Several mechanisms concerning the ion extraction in a spark source mass spectrometer have been described in the literature (*4–7*). Just as in the case of laser ionization (*8*, *9*), most of the attention is paid to the hydrodynamic acceleration of ions and to the acceleration of ions in a self-consistent electric field, because these two mechanisms have been thought to be the defining processes of ion extraction (*3*, *7*). Although acceleration in an external field with respect to the spark plasma has been rejected as a possible way of ion acceleration by some authors (*7*), it regained our attention when we were able to simulate ion trajectories in the spark source with the aid of SIMION (*10*), a powerful lens analysis program. With this program it was possible to explore the dynamic behavior of ions due to the residual oscillations of the electrical potential during a spark discharge.

CALCULATION OF ION TRAJECTORIES

SIMION has been used in this work to simulate the ion extraction from a radio frequency spark source mass spectrometer. In the conventional view concerning the ion extraction in an rf spark source, the spark box is essentially field free (apart from the weak penetration of the acceleration field through the exit slit). Since the electrical field existing between the electrodes during a spark discharge is alternating at a high frequency (ca. 1 MHz), it is assumed in the conventional view on the spark source that, averaged in time, no potential difference exists between the electrodes. The graphical representation of ion trajectories in such a configuration for the JEOL JMS-01-BM2 ion source is given in Figure 1; it demonstrates the focusing ability of the penetrating part of the acceleration potential. The external field can penetrate into the spark plasma between the electrodes up to the extent of the Debye length; therefore, only the ions from this region of the plasma will be affected. During plasma expansion this region will become larger and give rise to individual ions leaving the plasma. As a consequence, we started the ion trajectories not halfway between the two sparking electrodes but somewhat shifted toward the acceleration slit.

The assumption of a field free region in the spark box (time averaged) is not completely correct. Figure 2 shows how the potential varies just before and during an rf spark discharge (*3*). During the expansion of the spark plasma, an external alternating field (relative to the plasma) is present between the electrodes, having an amplitude of ca. 1000 V and a frequency of 10–25 MHz. Franzen (*6*) described this field to explain the extraction and energy distribution of the ions.

These data have been used to implement a time-dependent residual voltage on the electrode configuration shown in Figure 1. The effective voltage on the electrodes in the spark box can then be written as

$$U = U_0 + U_1 \sin(2\pi\nu t + \Delta\phi) \qquad (1)$$

where U_0 is the applied acceleration voltage, U_1 is the maximal amplitude of the residual voltage oscillation during spark discharge, ν is the frequency of these oscillations, and t and $\Delta\phi$ are the time and the phase angle between the departure of an ion trajectory and the residual potential oscillation.

If we take ν = 10 MHz, U_0 = 27 kV, U_1 = 1000 V, and $\Delta\phi$ = 1.65 rad, the calculation of the ion trajectories for $^{56}Fe^+$ (initial energy 10 eV) shows that the residual potential oscillations have a pronounced influence on the behavior of ions in the spark box, as presented in Figure 3. Variation of the phase angle affects the transmission of ions, shown in Figure 4 for $^{56}Fe^+$, where $\Delta\phi$ = 1.25 rad.

Since the argument of the sine in eq 1 changes with the same frequency as the residual potential oscillations, the transmission and subsequent detection of ions are largely time dependent (even if we assume a continuous production of ions during a discharge). Earlier time-of-flight measurements (*11*) indicated the possibility of such fluctuations in ion extraction. Sometimes selected ionic species could not be detected for a given discharge (single shot), and numerous time distributions of detected ions showed unexpected variations, which can be explained by the existence of the residual electrical field between the electrodes. Since ions departing with nontransmitting phase angles are deflected (Figure 4), the ion beam will "swing" across the exit slit, resulting in a time distribution of detected ions which displays an oscillation with a frequency ν (in this case 10 MHz).

It is surprising that the value of the optimal transmitting phase angle decreases with increasing mass and becomes

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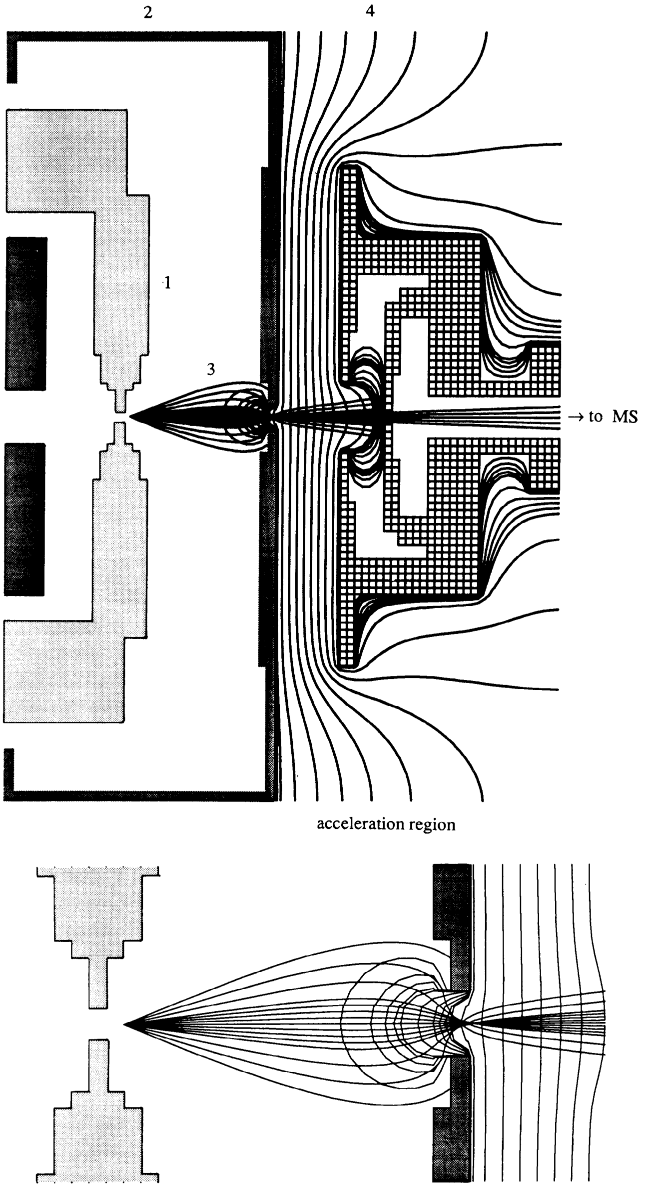

Figure 1. Top: ion trajectories for $^{56}Fe^+$, initital energy = 10 eV, conventional view: 1, electrodes; 2, spark housing (spark box); 3, ion trajectories; 4, equipotential lines. Dark gray, potential = U_0 V; light gray, potential = U V; hatched, potential = 0 V. Bottom: scale expansion of Figure 1, top.

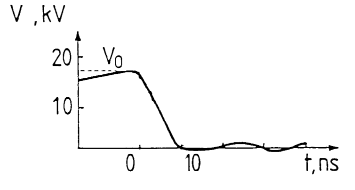

Figure 2. Variation of the potential just before and during spark breakdown (*3*).

virtually constant at high masses, as shown in Figure 5 for a broad mass range. For example, $^{12}C^+$ ions are transmitted at phase angle $\Delta\phi = 2.178$ rad. From this figure it should also be noticed that a change in phase angle (the dashed lines represent the outer limits of transmitting phase angles) is more critical in terms of transmission for lower masses, representing a real mass discrimination at low masses from an analytical point of view. The reason for increased susceptibility at low masses is that lighter ions are more affected by the residual potential oscillations on their path toward the exit slit, resulting in a larger amplitude of the oscillation in the ion beam.

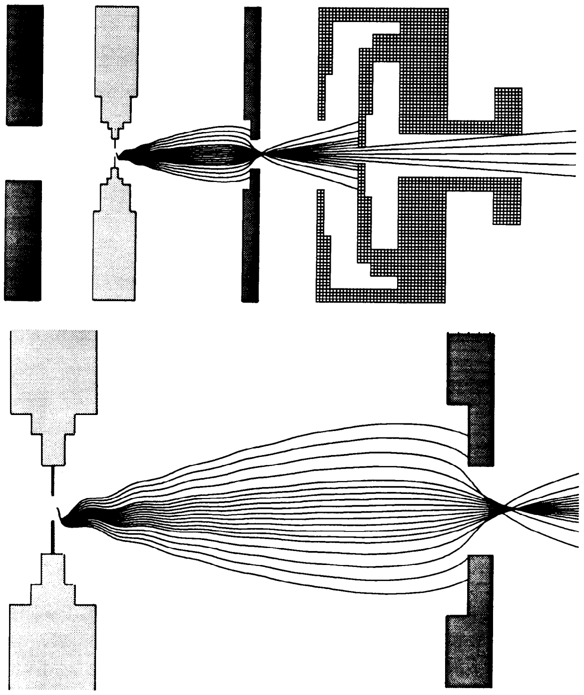

Figure 3. Top: ion trajectories for $^{56}Fe^+$, initial energy = 10 eV, $\Delta\phi$ = 1.65 rad, ν = 10 MHz. Bottom: scale expansion of Figure 3, top.

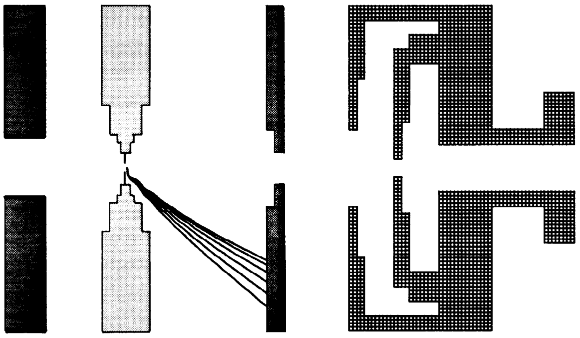

Figure 4. Ion trajectories for $^{56}Fe^+$, initial energy = 10 eV, $\Delta\phi$ = 1.25 rad, ν = 10 MHz.

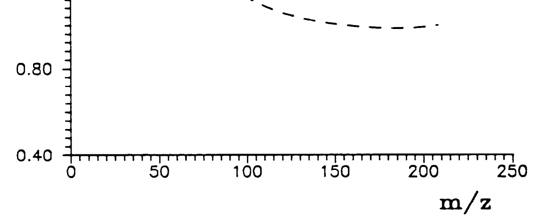

Figure 5. Phase angle for transmission as a function of *m*/*z*.

CONCLUSION

Calculations of ion trajectories in the ion source of a spark source mass spectrometer show that the residual electrical field between the sparking electrodes can have a large influence on the transmission of ionic species. So far no direct experimental evidence has been found for this effect, although time-resolved measurements support some of our predictions. Different masses are transmitted at different phase angles, and the critical interval of transmitting phase angles is larger for higher masses, indicating a mass discrimination toward lower masses. Modifications of the electric circuitry of the rf spark ion source that reduce the residual electric field oscillations during a spark discharge should lead to better and more stable ion transmission. In the view of new techniques (e.g., GDMS) this can contribute to make SSMS more competitive as an analytical instrument.

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