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Suspended Trapping Pulse Sequence for Simplified Mass Calibration in Fourier Transform Mass Spectrometry

David A. Laude, Jr.,* and Steven C. Beu

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712-1167

A new pulse sequence for Fourier transform mass spectrometry (FTMS) is demonstrated to simplify wide-band mass calibration through a self-regulating procedure that reduces any initial ion population in the trapped ion cell to a level below the space charge limit. The novel feature of the pulse sequence is the addition of an event following ionization during which the trap plates of the FTMS cell are grounded to permit the longitudinal efflux of excess ions from the cell. The actual ion population detected then depends not on the initial neutral population or ionization conditions, but rather on the suspending trapping delay time. At suspended trapping delays of 1-2 ms for both single- and dual-section trapped ion cells, the number of ions detected is reduced to a level at which the ion density electric field contribution to the effective cyclotron frequency is negligible. Low-part-per-million error mass calibration tables are generated when suspended trapping is applied to initial ion populations which extend 2 orders of magnitude beyond the space charge limit of the cell. This is contrasted with marked deterioration in mass calibration performance for identical initial ion populations if trapping voltages are sustained.

It is well documented in Fourier transform mass spectrometry (FTMS) that mass spectra derived from ion populations that exceed the space charge limit of the trapped ion cell are of poor quality. The effects of space charge include Coulombic line broadening (*1*), complications in mass calibration (*2-5*), and reduced dynamic range (*6-9*). If a stable and continuous supply of neutral sample is available and sufficient time exists to tune ionization parameters, ion populations generated with negligible space charge yield high resolution and high mass accuracy spectra characteristic of FTMS. More often, however, the neutral analyte population is transient, poorly controlled, or fluctuating, and preselected ionization conditions often yield the excessive ion populations responsible for space charge distortion. The consequence of a strong dependence of FTMS system performance on the initial ion population in the cell is that for many modes of sample introduction and ionization, FTMS operation is perceived as difficult or unreliable when contrasted with that of other mass analyzers. For example, the dynamic range for FTMS detection of chromatographic effluent is orders of magnitude smaller than for scanning mass spectrometers because ionization parameters established to acquire acceptable spectra at one neutral population will either reduce the detectable signal of smaller neutral populations or exceed the space charge limit for larger populations. FTMS application to desorption/ionization of solids is also unreliable because a transient gas-phase population must be sampled.

It is of interest then to develop reliable methods by which more difficult sampling regimes can be examined with FTMS. One approach presented here is the use of suspended trapping pulse sequences as a solution to the problem of generating acceptable ion populations from transient or fluctuating neutral populations. All suspended trapping techniques share the common feature that during at least one event in the FTMS pulse sequence the trapping voltages are altered (typically to ground potentials) to permit the longitudinal movement of ions to and from the analyzer cell. To date the primary function of suspended trapping is to gate externally generated ions into the trapped ion cell. This application has been demonstrated for both quadrupole (*10-12*) and electrostatic focusing (*13, 14*) external source instruments and for

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the differentially pumped dual-cell instrument marketed by Nicolet Analytical Instruments (*15*). Dunbar describes a different application of suspended trapping in which ion flight times from the cell are measured to determine the kinetic energy of photolytically created ions (*16*). In contrast, suspended trapping is used in the present work to control longitudinal ion motion between multiple potential wells along the path of the electron beam in the FTMS vacuum chamber and thereby permit a variety of analytically useful experiments for sensitivity and dynamic range enhancement, mass and kinetic energy selection, and improved mass calibration.

As first evidence of the facility of the suspended trapping technique, it is applied to the simplification of mass calibration procedures in FTMS. The cyclotron frequency of an ion is known to decrease with increased ion density. Gross first demonstrated that the ion cloud electric field in the cell mimics the behavior of the static electric trapping fields (*2*). Jeffries later developed a model that described space charge contributions to the equations of motion in the FTMS cell (*3*). Following from this work, McIver derived an approximate expression for effective cyclotron frequency (ref 4, eq 7) that included not only static magnetic and electric field terms, but also a third term that accounted for space charge. McIver (*4*) and others (*1*, *5*) then demonstrated that for a known ion population, mass calibration equations that correct for space charge can yield low-parts-per-million errors. In practice, however, the dependence of mass calibration on ion density makes routine mass accuracy measurements in large and variable ion populations unfeasible. Instead, the more common approach to accurate mass calibration in electron ionization FTMS has been to minimize the contribution of the ion density term by using reduced emission currents and short beam times. Unfortunately, the necessarily mild ionization conditions that yield low ppm mass errors often conflict with sensitivity and dynamic range requirements. As a result, practical applications of accurate mass measurement in FTMS are limited.

Suspended trapping provides an alternate approach to simplified mass calibration that also relies upon minimization of the ion density term in calibration equations. However, this reduction is accomplished not by altering ionization conditions but rather by eliminating excess ions formed during the ionization event which contribute to space charge distortion. In effect, an invariance to initial ionization conditions is achieved, which not only eases tuning procedures for generating low ppm error calibration tables of static neutral populations, but also provides the first reliable approach to accurate mass measurement for the many experiments in which neutral populations cannot be controlled.

EXPERIMENTAL SECTION

All experiments were performed on a mass spectrometer assembled with components that comprise the commercial FTMS-2000 marketed by Nicolet Analytical Instruments. Included on the system are the FTMS-2000 3.0-T magnet, dual cell, high-power excitation amplifier, preamplifier, cell controller, electron ionization assembly, and 1280 data station. Source and analyzer regions of the vacuum chamber are pumped with 700 L/s Alcatel Crystal 150 UHV diffusion pumps backed by 11 cfm Alcatel 2012A two-stage direct drive mechanical pumps. Base pressures in both chambers are in the low 10^{-9} Torr range as measured with nude Bayard-Alpert ion gauge tubes extended 1 m above the pump throat outside the magnetic field. The standard 2-mm conductance limit between source and analyzer trap plates permits a sample-dependent pressure differential of 200–500. Volatile samples are introduced to either source or analyzer chamber through Varian variable leak valves. Nicolet software is used to control all aspects of the FTMS experiments. The suspended trapping pulse sequence, written and compiled for execution as an experiment in the commercial software, is a modification of the general FTMS pulse sequence that includes a variable length suspended trapping event during which analyzer trap, source trap, and conductance limit plates are set equal to 0.0 V. This event is inserted following the electron beam event and prior to resonance ejection or excitation events.

Benzene and perfluorotributylamine (PFTBA) were used to characterize the new pulse sequence. Each was subjected to freeze–pump–thaw cycles before introduction through leak valves into the vacuum system. For single section cell experiments conducted in the analyzer chamber with the conductance limit set equal to the analyzer trap potential, sample was leaked through the source leak valve until an analyzer pressure of 1×10^{-9} Torr above base pressure was registered on the ion gauge controller (source pressures were between (2 and 5) $\times 10^{-7}$ Torr). For dual-cell experiments, sample was introduced to 2×10^{-9} Torr above background in the source vacuum chamber.

In all experiments, the commercial software single-resonance pulse sequence (SGL) was compared to the suspended trapping sequence for identical ionization, excitation, and detection parameters. Electron ionization with 70-eV electrons for beam times of up to 50 ms and requested emission currents of up to 50 μA produced initial ion populations of 10^3 to in excess of 10^6. Actual emission current through the dual cell measured at a collector plate was 20% of the requested current. An estimate of the number of ions generated during the beam event is calculated from the ion current, beam time, source pressure, neutral cross section, and ionization volume (*17*). Unless otherwise noted, 2-V trapping potentials were used except during the suspended trapping event when plates were grounded. Swept excitation over a 2.66-MHz bandwidth with a sweep rate of 3200 Hz/μs was followed by detection of an 800-kHz bandwidth (low mass cutoff of m/z 58). For experiments with benzene, 50 coadded scans of 16K data were acquired and then processed with addition of 16K zeroes, base-line correction, sine-bell apodization, and a magnitude-mode Fourier transform. For accurate measurements with PFTBA, 64K data were acquired and processed in a similar manner. Nicolet-supplied subroutines for determination of mass resolution at the half height (RES), relative peak intensity (CVA), and mass calibration of PFTBA (CL1) were used without modification. Mass measurement accuracy is presented as the 95% confidence level in hertz for the seven PFTBA fragment ions at m/z 69, 100, 131, 219, 264, 414, and 502.

RESULTS AND DISCUSSION

The justification for suspended trapping as a means to minimize space charge and thereby simplify mass calibration follows. During the ionization event, the instantaneous velocity of an ion is determined by its kinetic energy and by its position in both trapping and ion cloud electric fields. When suspended trapping commences, trapping fields disappear and ion flight from the cell depends upon the instantaneous longitudinal kinetic energy of the ion and Coulombic repulsive effects of the ion cloud. Early during the suspended trapping event when the ion density is highest, Coulombic repulsive effects can be significant and ions exit the cell at a rate faster than expected on the basis of time-of-flight considerations for ion kinetic energy alone. As the suspended trapping delay increases, an ion cloud with reduced kinetic energy and small local electric fields remains so that reestablished trap potentials will then constrain an ion population that does not exhibit space charge effects. Of course, selection of an optimum suspended-trapping time is not trivial because at long delays the spectral signal-to-noise (S/N) ratio deteriorates and mass discrimination results from the time-of-flight effect.

Suspended Trapping Studies of Benzene Molecular Ion. The molecular ion of benzene at m/z 78 was used to investigate ion flight during the suspended trapping event for both single and dual section cell designs in an FTMS 2000 vacuum chamber. Experiments were performed for both small, $\sim 10^4$, and large, $\sim 10^6$, initial ion populations. For the single-cell, low-density experiment, a 5-ms electron beam and 1.0-μA emission current through the cell were calculated to yield on the order of 10^4 benzene molecular ions. As indicated by the quality of the spectra for these conditions the total ion

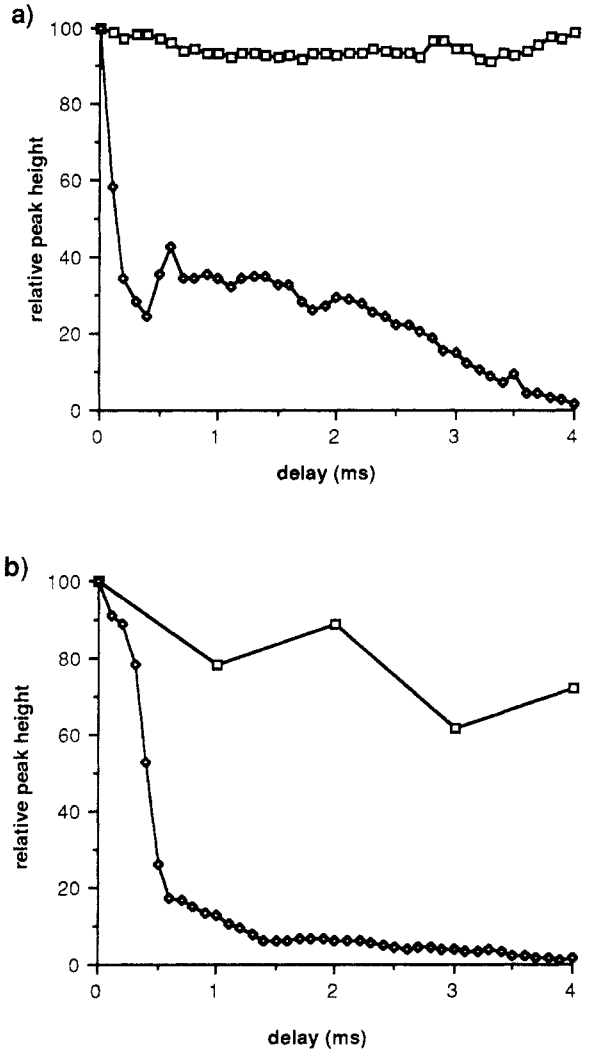

Figure 1. Ion flight measurements for benzene molecular ion in an FTMS single-section cell comparing suspended trapping, ◇, and conventional trapping, □. In part a, 10^3 to 10^4 m/z 78 ions are created during ionization. In part b, 10^6 m/z 78 ions are created during ionization.

population in the cell was within the space charge limit of the cell. For the single-cell, high-density experiment, a 30-ms beam event and 11-μA emission current created 60 times more ions with consequent deterioration in spectral quality through the cell; observable space charge effects with trap potentials maintained throughout the experiment included frequency shifts in excess of 250 Hz, a 10–20% reduction in mass resolution, severe peak shape distortion, and nonlinear peak intensities.

Ion flight during suspended trapping was first investigated for a single section cell experiment. For the low charge density experiment in Figure 1a, appreciable ion loss was not observed for continuously trapped ions because available nonreactive loss mechanisms such as ion evaporation (*18*) and ion neutral collisions were not significant on the millisecond time scale for the neutral pressures, ion populations, and trapping fields used. In contrast, ion loss from the trapped ion cell did occur during the suspended trapping event, although the rate of disappearance was much slower than expected and the detectable ion population in the cell was not exhausted for more than 4 ms. This result was surprising because a calculation of the one-dimensional root-mean-square velocity of benzene molecular ion at even thermal energies indicates all ions should exit the cell within a few hundred microseconds after the trap plates are grounded. The rapid initial loss, near 70% in less than 200 μs, was on a time scale associated with time of flight for thermal ions, but this loss was interrupted at longer delays and a steady ion population at 25% of the initial ion intensity was observed for about 1500 μs before a gradual erosion of the signal occurred.

The unexpected high ion retention at increased suspended trapping times is attributed to an influx during suspended trapping of ions in adjacent external wells and to the retention of low-energy ions due to small residual potentials that remain on the trap plates during suspended trapping. The magnitude and relative contributions of these two effects are a function of cell and filament assembly geometries, cell alignment, and cell cleanliness. They are described for this particular FTMS 2000 dual-cell design only briefly here, but in more general terms elsewhere (*19*).

The contribution of externally generated ions during suspended trapping arises from a serendipitous arrangement of cell trap plates and electron gun assembly that satisfies the geometry requirements of FTMS vacuum chambers in superconducting magnet systems. The series of six electrodes perpendicular to the applied magnetic field in the FTMS-2000 includes not only the two trap plates and conductance limit for the dual cell but also electrodes about 40 cm from the conductance limit at each end of the vacuum chamber, which serve as gate and collector for the electron beam, and an off-axis guide ring for the sample probe which is located 8 cm from the source trap plate. During the electron beam event two large potential wells are created in the high-pressure source region adjacent to the source trapped ion cell. One well, 30 cm in length, is formed between the collector plate and guide ring which are in electrical contact and maintained at 5 V during ionization. A second 8-cm well is created between the source trap plate, which is maintained at 2 V, and the guide ring. Ions formed in these reservoirs are transparent to the ion population in the dual cell during conventional experiments because the sustained trapping potential at the source plates partitions the wells. However, during suspended trapping experiments the reservoirs become a replenishing source of ions for the trapped ion cell. Direct evidence that the reservoir ions enter the cell during suspended trapping was obtained by applying a quench pulse to the trap plates during the electron beam event and then observing the influx of ions to the cell after a delay of several hundred microseconds. It should be mentioned that the off-axis orientation of the guide ring likely introduces a large radial electric field component to the motion of trapped ions in the reservoir, which reduces the effectiveness of the well for ion storage. More suitable external reservoir geometries are now being investigated.

A second source of the sustained ion signal at long suspended trapping delays appears to arise from ions formed in the trapped ion cell that possess insufficient kinetic energy to exit during suspended trapping because of residual charging on the plates. Evidence to support this assertion includes the following observations: (1) At increased pressures and following thermalization delays the fraction of ions that remain in the cell during suspended trapping increases, and (2) as trap plates become increasingly contaminated and more likely to exhibit charging, the storage time during suspended trapping increases. This ion retention, while undesirable for quantitative measurements (*16*), is advantageous in this analytical application. It suggests the use of suspended trapping delays in which the plate potentials are purposely set to a small nonzero value to reduce but not totally eliminate the ion population. This approach might then be implemented with vacuum systems for which the external reservoir is not feasible.

Single section cell suspended trapping experiments with benzene were repeated with initial populations of about 10^6 benzene molecular ions. As indicated in Figure 1b, the ion

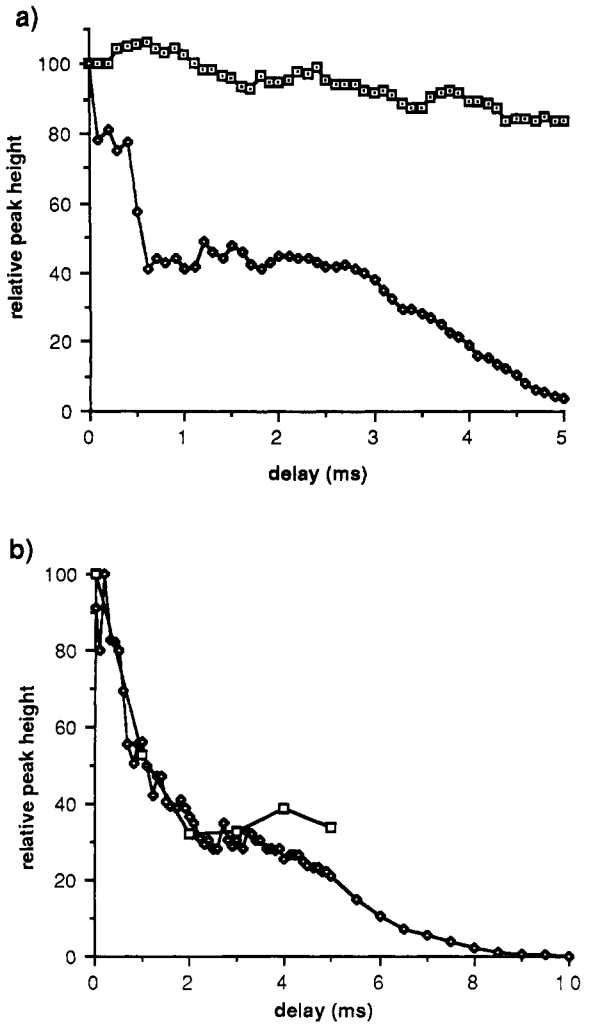

Figure 2. Ion flight measurements for benzene molecular ion in an FTMS dual cell comparing suspended trapping, ◇, and conventional trapping, □. In part a, 10^3 to 10^4 m/z 78 ions are created during ionization. In b, 10^6 ions are created during ionization.

flight profile during suspended trapping was similar to that observed for the low-density measurements with the exception that strong Coulombic repulsion in the dense ion cloud increased the initial rate of ion loss. Once again, however, a sustained ion population was observed, in this example at 5–9% of initial ion intensity between 1500 and 3500 ms, before disappearing. Of significance was the observation that for delays greater than 500 μs, benzene spectra for both high- and low-density experiments were similar in intensity and identical in mass resolution and frequency. This suggested an important advantage of suspended trapping pulse sequences, the opportunity to create an ion population for detection which is independent of initial ionization parameters and neutral populations.

The effects of suspended trapping on data acquired with the dual cell were next examined. Ion formation in the dual cell was performed under standard conditions with the conductance limit grounded to establish an equilibrium ion population between cells during the beam event. Flight of high- and low-density ion populations from the analyzer trap of the dual cell during the suspended trapping experiment is shown in Figure 2. The data are qualitatively similar to the single section cell measurements in that for both ion populations, initial loss is followed by a several millisecond period during which ion signal is sustained by ions from the reservoir.

Because ion density in the trapped ion cell decreases with increased suspended trapping delays, cyclotron frequencies should increase to equal those observed in the absence of space charge. This was investigated for the benzene experiments. For the data in Figure 1a and 2a, the low ion density cyclotron frequency was found to remain constant at increasing delays after ionization for both sustained and suspended trapping experiments. However, for the data in Figure 1b and 2b the high-density cyclotron frequencies at zero delay time decreased by 190 and 341 Hz, respectively, for single- and dual-cell experiments. For the conventional experiment at increasing delays after beam, this decreased frequency value remained. In contrast, by 700 μs into the suspended trapping delay a sufficient number of ions exited the cell to permit the effective frequency to return to the value observed at low ion densities.

Mass Calibration Studies of PFTBA. The suspended trapping data obtained for benzene molecular ion indicates that mass calibration with the suspended trapping pulse sequence should not require a correction for space charge. Moreover, because the suspended trapping delay levels the detected population, a single calibration table that accounts only for the magnetic field and radial electric trapping fields should be effective for any initial ion population without concern for space charge. Experiments were performed with PFTBA to confirm for a wide mass range the effects of suspended trapping on space charge contributions to shifts in cyclotron frequency and to assess potential benefits for accurate mass measurement. From the benzene data it would be expected that after about a 1-ms suspended trapping delay the remaining ion population would exhibit no adverse space charge effects. Further evidence in support of this contention was obtained from accurate mass data at both 1- and 9-V traps for an initial PFTBA ion population of several million (17 μA through the cell and a 30-ms beam). As shown in Figure 3, calibration tables generated after suspended trapping delays of 500 μs to 1 ms improved dramatically. For the 1-V trap experiment, mass calibration errors of ±5 ppm with confidence levels of 1 Hz were achieved, while for the 9-V trap experiment, 6-Hz 95% confidence levels for mass errors of less than ±10 ppm were obtained. Data in Figure 3a also indicate that calibration curves for the conventional pulse sequence at 1-V traps improve at increased delays to achieve a 15-Hz confidence level; one possible explanation is that the ion population in the cell decreases because of ion evaporation in the relatively low trapping fields.

Once it was demonstrated that improved mass calibration parallels the reduction in ion population for increased suspended trapping times, it was of interest to show that for a selected optimum suspended trapping time there is an invariance to initial ion population. Calibration tables were created for spectra acquired with both conventional and suspended trapping pulse sequences as beam time was increased for a 5-μA emission current. As shown in Figure 4a, as the ion population increased calibration tables deteriorated for the conventional pulse sequence, while good performance was maintained with suspended trapping. In a second experiment, emission current was increased from 500 nA to 50 μA at a constant 5-ms beam time to vary the ion population in the cell by 2 orders of magnitude. In Figure 4b the accurate mass data again demonstrate the inability of the calibration equation to correct for increased ion population. In contrast, the suspended trapping sequence levels initial ion populations below the space charge limit and retains low ppm error calibration tables even at high emission currents.

It is apparent from the data in Figures 3 and 4 that suspended trapping should simplify mass calibration for any set of ionization conditions. There are however difficulties in the application of suspended trapping that potentially detract from its general utility. Among the most serious limitations are decreased signal-to-noise ratio at long suspended trapping

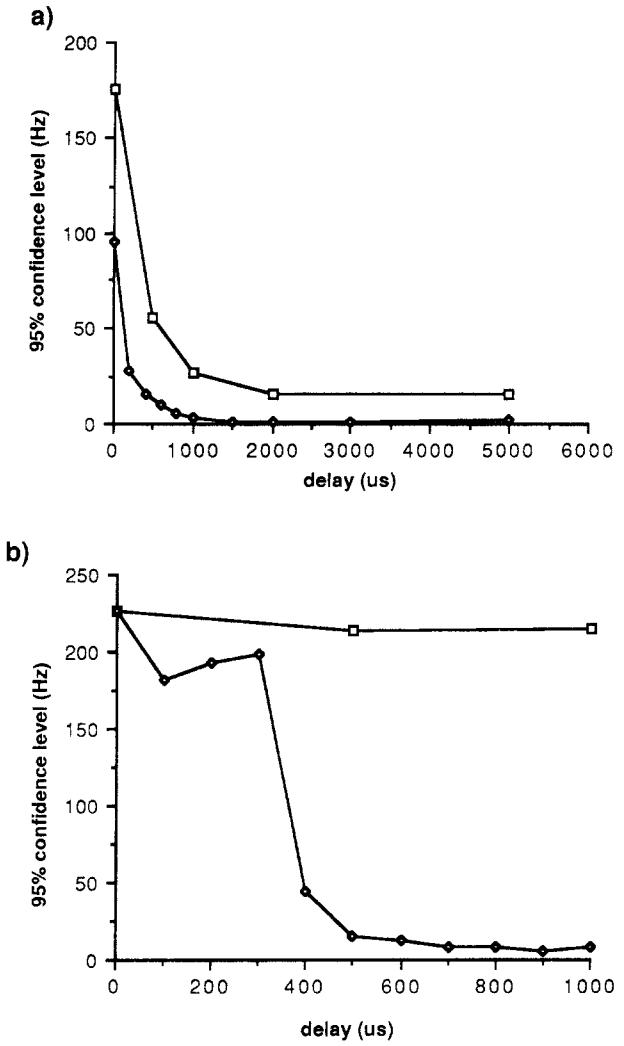

Figure 3. Mass calibration table quality at increasing delays during conventional, □, and suspended trapping, ◇, is determined for (a) 1-V and (b) 9-V trap potentials. The measure of performance is the 95% confidence level from mass calibration of PFTBA ions at mass 69, 100, 131, 219, 264, 414, and 502.

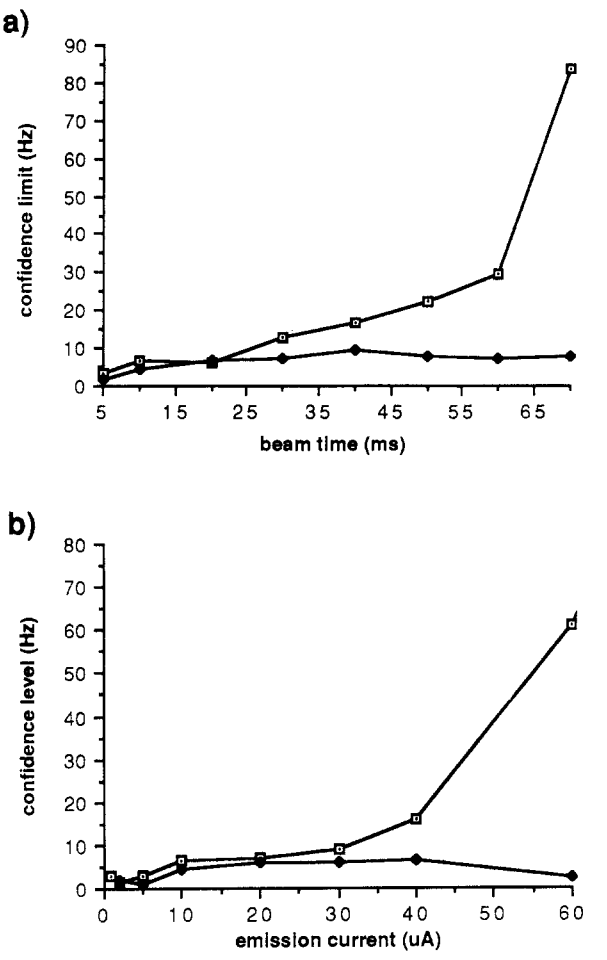

Figure 4. Mass calibration performance at a 1-ms suspended trapping time is determined for increasing ion populations with conventional, □, and suspended trapping, ◇. In part a the beam time is maintained at 5 ms while emission current is increased. In part b the emission current is maintained at 5 μA and beam time is varied.

times, loss of scan-to-scan quantitative information, an uncertainty in selecting a suspended trapping time that is effective for all initial populations, and the possibility of severe mass discrimination as low-mass ions preferentially exit the trapped ion cell. Fortunately, the large residual ion population detected in the cell over a several millisecond period assists in countering many of these problems. For example, examination of low-density single- and dual-cell data in Figures 1a and 2a indicates that at suspended trapping delays of 1–2 ms, the loss in signal is only 50–75% because of the continuous influx of ions from the neighboring well and the residual ions that cannot exit the trap. This modest sensitivity loss for static low-density neutral populations should be offset by using longer beam times and higher emission currents. For experiments in which the neutral population fluctuates, as in the detection of chromatographic effluent, it is expected that the combination of suspended trapping and intense ionization conditions will actually extend the working range in which high-quality spectra are generated at both high and low concentrations of neutrals.

The time-of-flight effect should lead to mass discrimination for extended suspended trapping delays as the lower mass ions are preferentially eliminated. This effect is observed, but is less pronounced than expected, again because of the countering effect of incoming ions from the adjacent well and residual retained ions. The degree to which skewing of peak intensities is exhibited and the appropriate conditions to counter the effect are a complicated function not only of initial spatial distribution and kinetic energy for the ion population, but also of the various electric fields established during the suspended trapping sequence. Figure 5 provides an interesting contrast of suspended trapping spectra that illustrates how changes in acquisition parameters can affect relative abundances in suspended trapping spectra. Although both spectra were acquired after a 1-ms suspended trapping delay for identical ionization conditions, the PFTBA relative peak intensities for a mass spectrum acquired with a 9-V trap are qualitatively similar to expected peak intensities, while the relative abundances for the spectrum acquired within a 1-V trap are grossly skewed toward higher mass.

The sole acquisition parameter for suspended trapping that determines the ion population during data acquisition is the delay during which trapping voltages are grounded. Thus, it is essential that a single delay time be found that will yield high-performance spectra independent of any initial ionization conditions. Again the presence of the long-lived residual ion population eases the selection of an appropriate delay. Without these ions, the FTMS signal would be depleted after a few hundred microseconds and selection of a suspended trapping delay time would be difficult. However, as the data in Figures 1 and 2 indicate, not only are ions observed in the cell in large numbers after several milliseconds independent of initial ion population, but for all cases selection of any delay between 1 and 3 ms yields nearly identical spectra. Of course other criteria in selecting the suspended trapping delay are

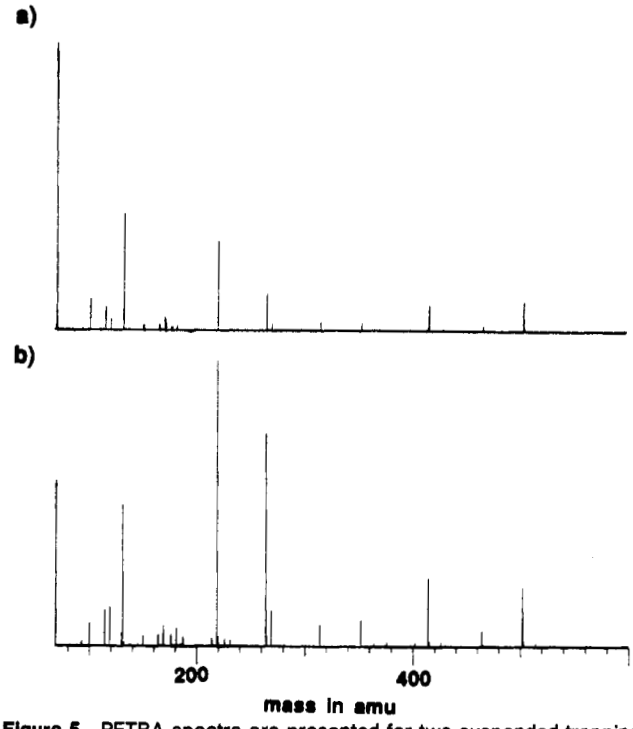

Figure 5. PFTBA spectra are presented for two suspended trapping FTMS experiments to contrast mass discrimination effects. The conditions for each case are identical except that a 9-V trap is used in part a and a 1-V trap in part b.

minimizing mass discrimination and maximizing signal intensity; for these reasons a 1-ms delay was used in this work.

Suspended trapping is a promising new approach to simplified mass calibration in FTMS because a single delay event obviates the need to precisely control initial ionization conditions. This should be an important advantage when accurate mass data is desired for neutral populations that are poorly controlled or transient, as for example during FTMS detection of chromatographic effluent. Suspended trapping is currently being applied to GC/FTMS as a means not only to improve the reliability of accurate mass measurement, but also to extend the qualitative dynamic range. Application of suspended trapping to a variety of signal enhancement and mass and energy selection experiments is also being investigated.

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