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Tandem Quadrupole/Time-of-Flight Instrument for Mass Spectrometry/Mass Spectrometry

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A new tandem mass spectrometer for MS/MS studies is described. The instrument consists of a quadrupole mass filter followed by a time-of-flight mass analyzer. A collision cell is located in the region between the two analyzers. Low-energy parent ions (<100 eV) are mass analyzed by the quadrupole and injected into the collision cell. Daughter ions from collision-activated dissociations (CAD) as well as unfragmented parent ions are accelerated by 1000 eV upon exiting the collision cell. These accelerated ions are then gated into the time-of-flight for mass analysis. Conventional mass spectra may be obtained either by operating the quadrupole in an rf-only mode, where it passes all ions, and using the time-of-flight analyzer or by scanning the quadrupole in the normal fashion and gating the time-of-flight analyzer continually on. Preliminary results are shown and potential improvements and applications are discussed.

The past several years have been a time of rapid growth in the area of mass spectrometry/mass spectrometry (MS/MS). It is now a standard technique in many laboratories. A recent review (*1*) and book (*2*) cover the analytical applications and other capabilities of MS/MS. As a result of the growing popularity of MS/MS and the demonstration of a wide range of studies to which it can be applied, much attention has been devoted recently to various instrumental configurations for MS/MS.

The initial several years of MS/MS were dominated by instruments of reverse geometry (BE), a magnet (B) followed by an electric sector (E) (*3*). An important feature of this instrument is its ability to measure kinetic energy releases of fragmenting ions (*4*). However, this also proves to be a disadvantage as the daughter ion mass resolution is poor due to the energy release (*5*). Improvements in daughter ion mass resolution were realized with the introduction of the triple quadrupole (QQQ) as an MS/MS instrument (*6, 7*). This development accelerated the interest in MS/MS due to the operational simplicity and scanning speed of quadrupoles. It also heralded the current era of instrumental development for MS/MS.

Shortly after the QQQ was developed, several EBE instruments were introduced (*8–10*). These instruments were designed to obtain high mass resolution on the parent ion with the first two sectors (EB), with the third sector used to analyze the daughter ions. A fourth sector (a magnet) was added to one of these instruments, making an EBEB instrument in order to achieve better mass resolution on the daughter ions (*10*). Hybrid MS/MS instruments combining both sectors and quadrupoles followed these instruments (*11*). The advantages of these hybrid instruments lie in the better parent ion mass resolution they have over quadrupole-based instruments and the increased daughter ion mass resolution compared to sector instruments.

A common feature of all the above configurations is that they are scanning-type instruments and as such can only detect one MS/MS daughter ion at a time. Among instruments that are based entirely upon sectors and/or quadrupoles, the only exception to this is a BB-type instrument which uses a spacial array detector to observe a portion of the MS/MS spectrum simultaneously (*12*). MS/MS has been demonstrated recently on a FTMS instrument where all the daughter ions are detected simultaneously in the frequency domain (*13*). Perhaps of more practical interest to the analytical chemist is the recently described magnetic/time-of-flight (BT) instrument (*14, 15*). Contrary to the previously mentioned MS/MS configurations this instrument performs simultaneous analysis of parent and daughter ions instead of tandem analysis. Theoretically, because MS/MS spectra of all the ions in a mass spectrum can be acquired in a single sweep of the magnet, significant improvements in speed or signal to noise should result. While this is an exciting prospect, there are some limitations to this configuration for certain experiments (vide infra) which led us to develop the tandem quadrupole/time-of-flight (QT) instrument described in this article.

EXPERIMENTAL SECTION

A schematic of the instrument is shown in Figure 1 along with a positive ion acceleration scheme. The sample is introduced on the probe which can be operated from near 0 V to greater than 50 V with most experiments herein being performed at a probe voltage of 32 V. A source developed at Oak Ridge (*16*) focuses the ions from the probe into the quadrupole. The quadrupole and its associated electronics are a UTI Model 100C. The electronics have been slightly modified to allow operation in an rf-only mode as a front panel option. The entrance and exit apertures of the quadrupole presently used are 3 mm.

Upon exiting the quadrupole the ions are focused into a 10-mm collision cell by an einzel lens. The ions exiting the collision cell are then accelerated by a four-element lens into a drift region of approximately 50 cm. Because the quadrupole is operated at ground potential, the drift region has to be electrically floated at the accelerating potential, typically −700 to −1000 V for positive ions. Ion detection is performed by a Galileo Model 4830 channeltron, which is operated at approximately −2 kV. Two guard rings held at the same potential as the drift region are mounted directly in front of the channeltron to minimize the length of the voltage gradient between the drift region and channeltron. A set of deflectors is mounted on the last of the accelerating lenses to gate the ions into the drift region for time-of-flight analysis. One deflector is continually held at the drift region potential while the other is pulsed from approximately 150 V less than the drift region potential up to that potential. The normal "on" pulse width used in this study is 500 ns.

Figure 2 shows a diagram of the detection and timing scheme used. A free-running pulse generator is used to trigger a delay generator. The output of the delay generator simultaneously triggers the gating pulse for the deflectors and provides a start pulse for a time-to-pulse height converter (TPHC). The stop input of the TPHC is connected to the channeltron via a 100-MHz discriminator. When an ion is detected the TPHC is stopped and the amplitude is output to a multichannel analyzer (MCA). The MCA is operated in a pulse-height analysis mode, so that the data are collected as flight time (mass) vs. abundance. In this configuration only one ion per TOF pulse can be detected. However, with the ion currents used in this study the probability of having more than one ion per TOF pulse is extremely low.

In normal operation the pulse generator is run at a rate of 10–30 kHz and the delay generator is operated with no delay. However,

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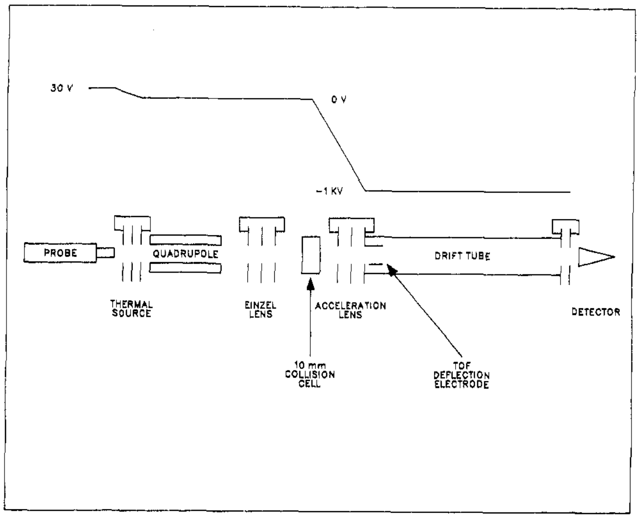

Figure 1. Schematic of the tandem quadrupole/time-of-flight (QT) instrument and acceleration scheme used for positive ions.

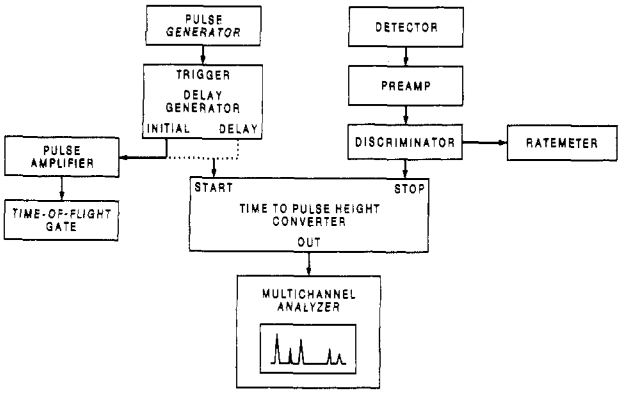

Figure 2. Diagram of the detection scheme used with the QT.

the delay generator can be used to delay the start trigger to the TPHC in order to expand certain portions of the spectrum. The exceptions to this mode of operation are when the filament is pulsed to simulate a transient event and in the operation of the system as a tandem time-of-flight/time-of-flight MS/MS instrument. In these cases the initial pulse ejects ions from the source region into the quadrupole; the delayed pulse gates ions within a selected time window into the drift tube.

All samples discussed in this paper were introduced on a thermal desorption sample probe that has been previously described (*17*). In the present configuration the temperature of the filament cannot be measured, but from previous results we estimate that the low-temperature desorption occurs at filament temperatures less than 400 °C (*18*). A few experiments were performed at high filament temperatures (estimated at 1500–2000 °C). In these studies sample that had been initially evaporated off the filament at low temperatures and deposited on source plates was reevaporated by radiative heat from the filament and ionized by the hot filament (*19*).

A 6-in. oil diffusion pump is used to pump the system. The base pressure of the system is ca. 1×10^{-6} as measured by a Bayard–Alpert ion gauge located above the throat of the pump. For collisionally-activated dissociation (CAD) MS/MS experiments, air was introduced into the collision chamber with a Granville–Phillips variable leak valve. The actual collision cell gas pressure cannot be measured at present, so gas was leaked into the collision chamber until the system ion gauge indicated pressures from 2.5×10^{-5} torr up to 1×10^{-4} torr.

RESULTS

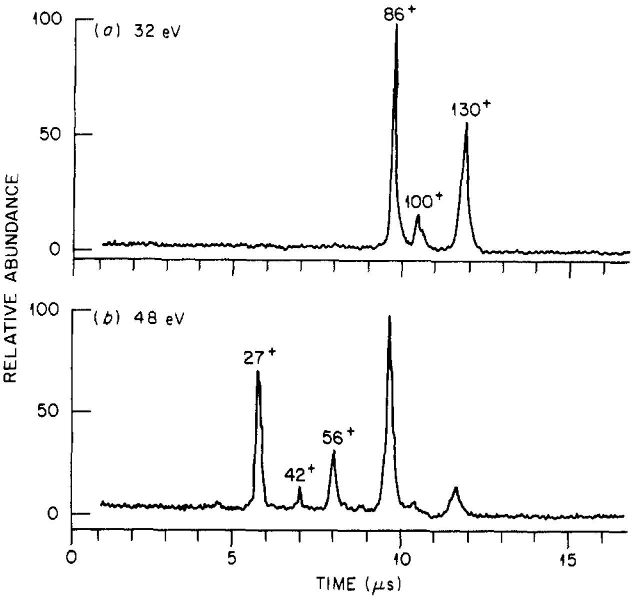

Figure 3. MS/MS spectra of *m/z* 130 from tetraethylammonium bromide at a collision gas pressure of 5×10^{-5} torr. (a) Collision energy of 32 eV; (b) collision energy of 48 eV.

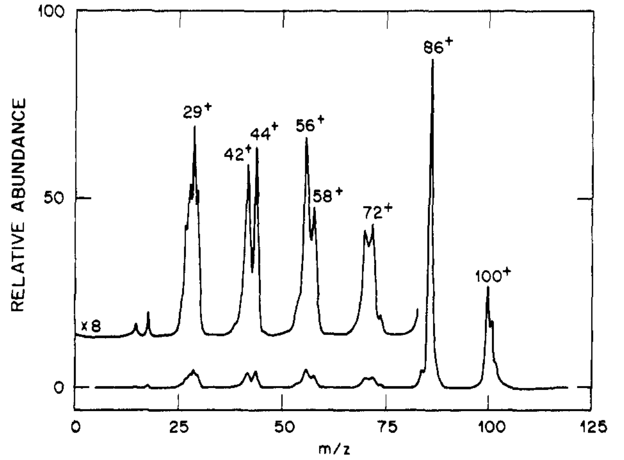

Figure 4. MS/MS spectrum of *m/z* 130 from tetraethylammonium bromide obtained on a triple sector instrument at a collision energy of 10 000 eV. The parent ion (*m/z* 130) is not shown as it is approximately 2 orders of magnitude more abundant than the fragments as is common in high-energy CAD spectra.

Figure 3 shows MS/MS spectra of the cation from tetraethylammonium bromide formed at high filament temperature. These spectra were acquired at laboratory collision energies of 32 and 48 eV and a system pressure of 5×10^{-5} torr. They show the expected behavior of increased fragmentation with increased collision energy (*7, 20*). For comparison, Figure 4 shows the high-energy CAD spectrum of this compound obtained on an EBE instrument in our laboratory. It was found during the course of this work that thermally desorbed quaternary ammonium and phosphonium ions are very stable and thus can require considerable collision energies to induce fragmentations. As the internal energy acquired by the ion is assumed to be dependent upon the center-of-mass collision energy (*21*), for a given set of experimental conditions higher mass ions will receive less excitation in the collision process. This was demonstrated by the fact that the onset of fragmentation for tetramethylammonium cation (*m/z* 74) was at a laboratory collision energy of about 7 eV while triphenylmethylphosphonium cation (*m/z* 277) showed no fragmentation even at a laboratory collision energy of 32 eV, although this difference is not necessarily due entirely to the amount of collisional excitation. Similar stabilities in low-energy collisions have been reported for aromatic species like $C_6H_6^+$ and $C_7H_7^+$ (*22*) where multiple bonds must be broken in the fragmentation process but not for simple single bond species like these quaternary compounds.

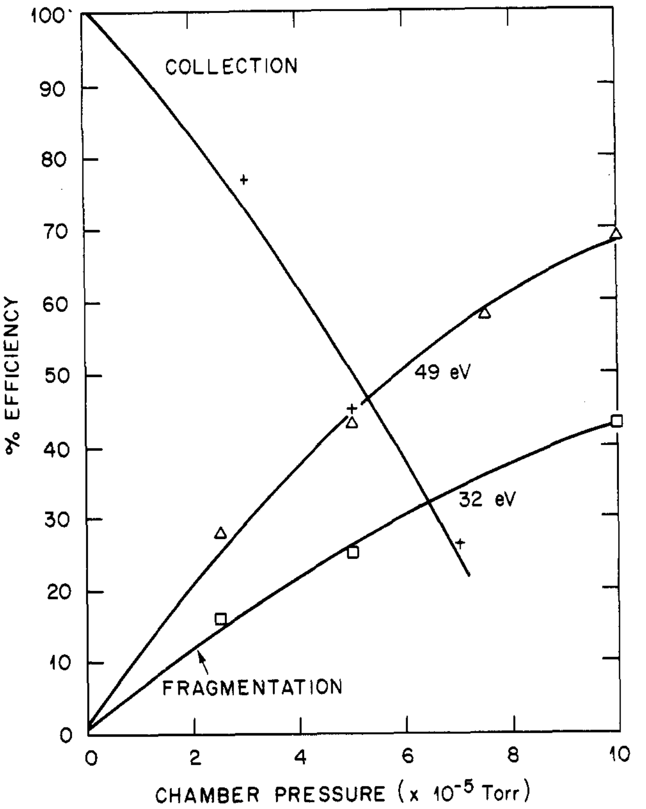

Figure 5. Plot of fragmentation efficiency vs. pressure of *m/z* 74 from tetramethylammonium bromide at collision energies of 32 and 49 eV and the collection efficiency at 32 eV.

In addition to collision energy, the collision gas pressure affects the amount of fragmentation (*7*). Figure 5 shows a plot of fragmentation efficiency vs. pressure at two different ion energies for the intact tetramethylammonium cation. The fragmentation efficiency has been defined as the sum of the fragment ion current divided by the total ion current exiting the collision region. As has been shown with other instruments (*6, 11*), the fragmentation efficiency increases with pressure. The collection efficiency was observed to be somewhat dependent upon the deflection and focusing voltages as well as collision energy and acceleration potential. The collection efficiency curve shown is for averge operating conditions. (The collection efficiency is the total ion current exiting the collision region dividing by the total ion current entering the collision region.) With the system studied here, the collection efficiency decreases at a somewhat greater rate than the low-energy CAD previously described (*6, 11*) but still not as rapidly as in the high-energy CAD experiment (*23*). However, this greater rate of decrease in collection efficiency compared to other low-energy CAD results may be due in part to the stability of the ions used in this study (vide supra).

The collection efficiency is related to the transmission of the TOF portion of the instrument; the uncollected ions are probably lost to a great degree by scattering out of the acceptance angle of this analyzer. Without any collision gas, 80–100% of the expected ion current, corrected for the duty cycle of the TOF, is detected. Thus, for a continuous ion current out of the ion source, approximately 0.5% of the total ion flux passed through the quadrupole will be detected during pulsed operation. The variation in transmission is a function of the temperature of ionization. At low filament temperatures lower transmission occurs (80%) while at higher filament temperatures, the transmission increases. This may be due to the location of ion formation, but further study is necessary.

One application that this instrument should be well suited for is the acquisition of MS/MS spectra of transient events, such as pulsed ionization, where the data acquisition can be synchronized with the ionization. To demonstrate this, the sample filament was pulsed to simulate a pulsed ionization event. The voltage on the filament was pulsed from 0 to 32 V for 2.5 μs to produce packets of ions that were extracted into the quadrupole. The rest of the instrument was operated in the normal manner except that the 500-ns drift tube deflection pulse was delayed from the filament pulse by the amount of time it took the ions to travel from the filament to the deflector. In theory, this is analogous to doing tandem time-of-flight/time-of-flight MS/MS, and data were collected in this mode by operating the quadrupole in the rf-only mode. However, the quadrupole is needed to achieve adequate parent ion mass resolution under the present configuration and conditions. Figure 6a demonstrates the ability of the QT to acquire a MS/MS spectrum of a simulated transient, with the tetramethylammonium cation selected as the parent ion.

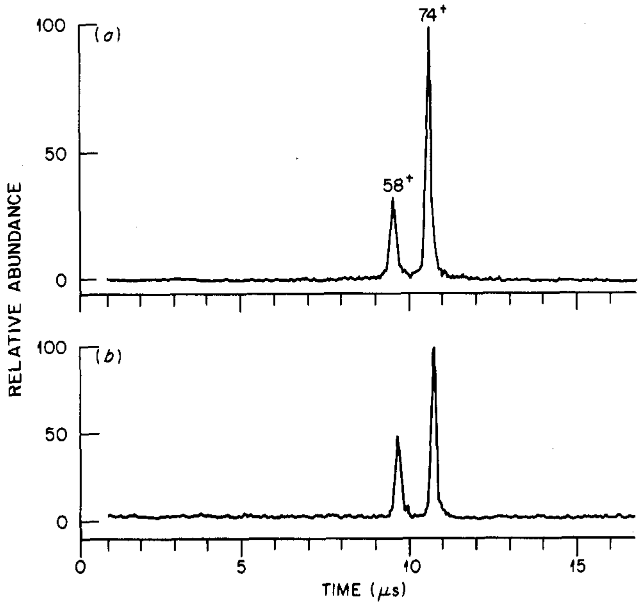

Figure 6. (a) MS/MS spectrum of *m/z* 74 using pulsed ionization, and (b) MS/MS spectrum of same ion taken in 10 s with a parent ion current of 2.4 × 10^{-15} A.

Figure 6b is an example of the ability of QT to rapidly obtain MS/MS spectra on continuous, low-level signals. Again, tetramethylammonium cation is the sample. This spectrum was obtained in 10 s on a parent ion flux of 1.5 × 10^4 ions/s (~2.4 × 10^{-15} A). This flux includes 4.5 × 10^2 counts/s of background noise because this spectrum was obtained at a high filament temperature and there is a line of sight from the filament to the detector. A similar spectrum was obtained in the same amount of time with a signal-to-noise ratio of about 5 using a parent ion flux of 500 ions/s.

As can be seen from the spectra in Figures 3 and 6, the parent daughter ion mass resolution is not very good. This is due in part to the fact that the system was assembled with existing hardware only to test the feasibility of operation, and thus little effort was made to optimize many parameters. It was note that a sharp maximum in resolution was obtained at an accelerating voltage of 1000 V. This is probably due to space focusing associated with the acceleration scheme (*24*). Resolution of the daughter ions is somewhat poorer than that of the parent ions due to kinetic energy released upon fragmentation. Possible methods for improvement of the mass resolution are discussed elsewhere (vide infra).

DISCUSSION

Comparison of the QT to the BT. Because a motivating factor for the development of the QT was the exciting prospects of the BT instrument (*14, 15*), it is informative to compare some of the properties of the QT to those of the BT. A major consideration that led to the development of the QT is its ability to acquire daughter ion spectra (the most common type of MS/MS spectra) without scanning the quadrupole. This is in contrast to the BT where the magnet has to be scanning to acquire any type of MS/MS spectrum. Thus, the QT configuration is much more convenient for acquiring daughter ion MS/MS spectra of a few ions in a mass spectrum, where all that is required is setting the quadrupole to the parent ion mass, vs. the necessity for acquiring a complete data matrix with the BT and then extracting the desired daughter ion spectra. Thus, for analyses where only a few daughter ion spectra are desired, the QT will have an advantage over the BT in the amount of time necessary to obtain a spectrum of a given signal to noise or conversely in signal to noise for a given amount of spectral acquisition time, all other factors being equal.

Another area in which the QT has an advantage over the BT is in parent ion resolution. The parent ion resolution in the QT is determined solely by the quadrupole, whereas in the BT the parent ion resolution is a function of the kinetic energy released during fragmentation. This problem is analogous to that encountered on conventional sector instruments when a linked scan at constant B/E is performed. However, since a complete data matrix is acquired with the BT instrument, this resolution problem may be alleviated in simple cases by peak centroiding or in more complex cases by advanced algorithms. Also, these peak shapes can sometimes be used to provide additional information. The QT's advantage in parent ion resolution is counterbalanced by its inferior daughter ion resolution; however, this should be at least partially correctable by instrumental means (vide infra).

Another difference between these two instruments is the energy at which the collision-activated dissociation occurs. The QT operates at low CAD energies while the BT uses high CAD energies. Each has advantages and disadvantages. The low-energy CAD typically gives increased efficiency in fragmentation and collection but is much more sensitive to changes in collision gas pressure than high-energy CAD.

Two other minor areas worth mentioning are the ease of computer control and mass range. Quadrupoles are more easily controlled by computer than magnetic sectors. This is especially true when peak hopping rather than scanning is desired. However, magnetic sectors have much greater mass ranges than quadrupoles. Whether this advantage is of practical importance is open to question though, because the BT's problem with parent ion resolution increases with mass.

Possible Instrumental Improvements. At present, the daughter ion resolution is the area most in need of improvement. As mentioned above, some improvement should be achieveable by more careful construction of the time-of-flight portion of the instrument and by extending the length of the drift region. In addition to this, there are several other methods which have been used to improve resolution in conventional TOF instruments which may be applicable to the QT. These methods include velocity and space compaction by varying the acceleration field with time (*25*) and velocity compensation via ion reflection (*26*).

Another option that would help improve resolution and provide additional capabilities would be the addition of an electric sector to the time-of-flight portion of the instrument. This would allow the option of doing high-energy collisions with daughter ion analysis then performed by scanning the electric sector providing data exactly as would be obtained on a BE geometry instrument. The only operating changes required to go from low-energy TOF analysis to high-energy E analysis in a configuration such as this would be floating the collision cell and reversing the functions of the lens systems prior and subsequent to the collision cell (i.e., accelerating the ions between the quadrupole and the collision cell and then subsequently focusing them). Of course, in either case it would be necessary to float the electric sector at the accelerating potential.

Enhancement of the performance of the QT system could also be achieved by using an rf-only quadrupole for the collision cell. This should increase the collection efficiency to a level comparable to the triple-quadrupole instruments and also reduce the dependence of the collection efficiency on the operating parameters.

The detection system of the instrument is another area where improvements are possible and necessary for optimum operation. At present, only one ion per TOF gating pulse can be detected. This is no problem with the low ion currents used in the above examples since the probability of having more than one ion per gate pulse is very small. However, for larger ion currents that would be expected with EI or CI sources, this situation is not acceptable. There are two recent developments that are applicable to this situation. The first uses a similar detection scheme except that a time-to-pulse height converter with multiple stop pulses (>30) per start pulse can be used, allowing detection of more than one ion per gating pulse (*27*). This system will work well when time is not a critical factor, as there still is a delay in getting the spectrum from the MCA to a data file. The other alternative detection scheme does not suffer from this problem. This is an integrating transient recorder with high-speed data transfer that is being developed by the group that conceived the BT instrument (*14*). This device will be of great value, not only to instruments such as the BT and QT but for general TOF analysis.

Potential Applications. The QT can be used as any normal MS/MS instrument; however, there are certain applications where it has definite advantages over scanning-type instruments. One such area is where pulsed ionization is used (e.g., laser desorption). The first laser desorption MS/MS experiment performed by using conventional instrumentation required ca. 30 min of data acquisition to get reasonable signal to noise (*28*). When a multistop time-to-pulse height converter detection system was used with the QT, this data acquisition time could be reduced considerably. It has recently been shown that laser desorption under chemical ionization conditions increases the length of time ions are observed per laser pulse but, at best, only to a few seconds (*29, 30*). In one of these studies (*30*), complete MS/MS spectra on a triple quadrupole system could be obtained on the longer lived signals. Thus, the QT should be able to provide similar data on these and shorter lived signals obtained from a single laser shot.

Another area where the QT configuration may be of great value is in combination with gas chromatography. GC/MS is a routine analytical tool now, but GC/MS/MS has seen very limited use and then only as a screening procedure for compounds selected in advance. This is due to the time constraints of the GC relative to the scanning time necessary to obtain a complete MS/MS data matrix on conventional MS/MS instruments. Since the QT greatly reduces the time necessary to obtain a spectrum, GC/MS/MS may become feasible in the same manner as postulated for the BT (*14, 31*). As an example, the spectrum shown in Figure 6b was obtained in 10 s with a parent ion current of ca. 2×10^{-15} A. Increasing that ion current by an order of magnitude decreased the data acquisition time by an order of magnitude to 1 s, for similar signal to noise. By extrapolation, for an ion current in the range of 10^{-11}, an MS/MS spectrum should be obtainable in a millisecond with an appropriate detection system (*31*), and thus a wide mass range of parent ions can be sampled in 1

s. A recent paper goes into this subject in very good detail (*31*).

CONCLUSION

The tandem quadrupole time-of-flight instrument has the potential to be a very useful and simple means to perform MS/MS experiments. It has a unique advantage in obtaining daughter ion MS/MS spectra on transient species such as those produced by pulsed laser ionization methods and has the potential to allow MS/MS to be combined on-line with chromatographic methods. By the addition of an electric sector in the TOF portion, this instrument could be very flexible in that access to both low- and high-energy CAD MS/MS would be possible.

ACKNOWLEDGMENT

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Field Desorption Mass Spectra of Pyridinium Oxime Salts with Rapidly Heated Emitter

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Mass spectral data of a few pyridinium oxime salts are reported. These thermally labile salts did not give consistent mass peaks in the molecular ion region with slowly heated FD technique. Rapid heating of the activated emitter at a rate of 15–25 mA/s in the field desorption/field ionization mode gave rise to cationized molecular ion peaks along with other peaks that facilitate identification of molecular ions of these salts in the concentration range 1–10 μg/mL.

Mass spectral analyses of mono- and diquarternary ammonium and phosponium salts are reported in the literature using field desorption techniques (*1*, *2*). More recently secondary ion mass spectrometry (*3*) and FAB (*4*) have also been used with success. In all the above cases the salts have been desorbed and ionized either as di- or monocations. Our experiments with a few pyridinium oxime salts in conventional FD technique could yield the monocation species. In a bid to see if the salt molecule as a whole can be desorbed and made available for giving mass spectral peaks, we utilized rapid heating of the emitter as a means of volatility enhancement, as explained by Beuhler et al. (*5*) and followed by many later (*6*) including P. J. Derrick et al. (*7*), who employed very rapid heating in the field desorption (FD) mode to obtain mass spectra of high molecular weight saccharides.

Because heating of the FD emitter is only for activation and facilitating migration of molecules, normal FD is generally run with slow heating of the emitter to find best anode temperature/best emitter temperature. With pyridinium oximes slow heating of the emitter (at the rate of 1–5 mA/min) mainly gave rise to fragments with monocationic species in some cases. In this paper we describe the results obtained by rapid heating (at the rate of 15–20 mA/s) of a activated emitter in a con-

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