

Proton transfer reaction ion trap mass spectrometer

Peter Prazeller¹, Peter T. Palmer², Elena Boscaini³, Tom Jobson¹
and Michael Alexander^{1*}

¹Pacific Northwest National Laboratory, 3020 Q Avenue, K8-93, Richland, WA 99352, USA

²Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, CA 94132, USA

³Institute of Ion Physics, Innsbruck University, Technikerstr. 25, 6020 Innsbruck, Austria

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Proton transfer reaction mass spectrometry is a relatively new field that has attracted a great deal of interest in the last few years. This technique uses H_3O^+ as a chemical ionization (CI) reagent to measure volatile organic compounds (VOCs) in the parts per billion by volume (ppbv) to parts per trillion by volume (pptv) range. Mass spectra acquired with a proton transfer reaction mass spectrometer (PTR-MS) are simple because proton transfer chemical ionization is 'soft' and results in little or no fragmentation. Unfortunately, peak identification can still be difficult due to isobaric interferences. A possible solution to this problem is to couple the PTR drift tube to an ion trap mass spectrometer (ITMS). The use of an ITMS is appealing because of its ability to perform MS/MS and possibly distinguish between isomers and other isobars. Additionally, the ITMS duty cycle is much higher than that of a linear quadrupole so faster data acquisition rates are possible that will allow for detection of multiple compounds. Here we present the first results from a proton transfer reaction ion trap mass spectrometer (PTR-ITMS). The aim of this study was to investigate ion injection and storage efficiency of a simple prototype instrument in order to estimate possible detection limits of a second-generation instrument. Using this prototype a detection limit of 100 ppbv was demonstrated. Modifications are suggested that will enable further reduction in detection limits to the low-ppbv to high-pptv range. Furthermore, the applicability of MS/MS in differentiating between isobaric species was determined. MS/MS spectra of the isobaric compounds methyl vinyl ketone (MVK) and methacrolein (MACR) are presented and show fragments of different mass making differentiation possible, even when a mixture of both species is present in the same sample. However, MS/MS spectra of acetone and propanal produce fragments with the same molecular masses but with different intensity ratios. This allows quantitative distinction only if one species is predominant. Fragmentation mechanisms are proposed to explain the results. Copyright © 2003 John Wiley & Sons, Ltd.

Proton transfer reaction mass spectrometry is a successful technique for trace gas analysis of volatile organic compounds (VOCs) with applications in various fields ranging from atmospheric chemistry to breath analysis and food chemistry. Details associated with the instrumentation and applications are described elsewhere.^{1–5} Briefly, a hollow cathode ion source is used to generate H_3O^+ reagent ions from water vapor. These hydronium ions are introduced into a drift tube reaction chamber along with a constant flow of a gas sample of interest. Compounds with proton affinities greater than that of water are ionized through proton transfer reactions following collisions with the H_3O^+ ions. This occurs for most VOCs such as aromatic hydrocarbons, aldehydes, ketones, acids, and alcohols, but not for atmospheric gases such as O_2 , N_2 , and CO_2 . The ions resulting from proton transfer reactions are extracted at the end of

the drift tube and are analyzed using a linear quadrupole mass spectrometer.

One of the primary advantages of this technique is that chemical ionization via proton-transfer reactions is a soft form of ionization that produces predominantly protonated molecules and relatively few fragment ions, reducing the complexity of the mass spectra. Although derived from large, laboratory-based flow drift tube instruments,^{6,7} current versions of the proton transfer reaction mass spectrometer (PTR-MS) are field-portable. Measurements are online and can have detection limits of approximately 10 pptv without any preconcentration. These instruments have proved to be at least as sensitive as conventional direct sampling MS techniques for analysis of VOCs in air.^{8–10}

One major drawback to PTR-MS measurements is that specific identification of compounds is problematic.¹¹ The only information available is the molecular mass (m/z), but there may be a variety of substances associated with one mass-to-charge ratio. Additionally, the spectra might be complicated due to mass overlap from cluster ions and

*Correspondence to: M. Alexander, Pacific Northwest National Laboratory, Mail Stop K8-93, P.O. Box 999, Richland, WA 99352, USA.
E-mail: michael.alexander@pnl.gov

fragment ions that are produced by protonation of some molecules. Although the mass spectra are less complex than those obtained with other, harder forms of ionization such as electron impact ionization or charge transfer, the presence of isobaric species can still lead to ambiguous or incorrect identifications. In select cases, fragmentation of species due to ionization can be helpful in distinguishing between isobaric species. This has recently been described for ketones, aldehydes and unsaturated alcohols by Buhr *et al.*¹² Another means to overcome this identification problem is by coupling a gas chromatography (GC) column to the PTR-MS.^{13–15} However, using GC results in the loss of the real-time measuring capabilities of the instrument.

Another method for resolution of isobars is to use an ion trap mass spectrometer (ITMS) with MS/MS capability. This concept has been demonstrated previously using laboratory-based flow reactors as ion sources for an ITMS.^{16,17} A flow reactor coupled to an ITMS has also been deployed in an aircraft for real-time atmospheric measurements.^{18,19} We have recently succeeded in coupling a small hollow cathode and drift tube source to an ITMS, and report the first results from this field-portable proton transfer reaction ion trap mass spectrometer (PTR-ITMS) here. Results are presented for the performance in terms of sensitivity and for the resolution of isobaric interferences encountered in proton transfer reaction mass spectrometry. These isobars can be resolved with other ionization methods, chemical or otherwise, but complete discussion of these alternate ionization schemes is beyond the scope of this paper.

Characteristics, and advantages and disadvantages of a conventional ITMS are well documented.^{20–24} We focus here on ITMS characteristics that are particularly relevant to an ITMS with a proton transfer reaction drift tube as an external ion source. The use of a quadrupole ion trap mass analyzer in lieu of a linear quadrupole to determine m/z of the protonated molecular species generated within the drift tube has two major advantages. The first advantage is a much higher duty cycle at each m/z acquired in the mass spectrum. In normal use, a linear quadrupole dwells on one m/z at a time and ignores the rest, so a large fraction of ions generated in the drift tube are not measured at all. With a linear quadrupole the duty cycle is given by:

$$t_{\text{dwell}} / (n(t_{\text{dwell}} + t_{\text{dead}}))$$

where t_{dwell} is the dwell time for a single mass peak, t_{dead} is the dead time required to switch the quadrupole from one m/z value to the next, and n is the number of m/z values monitored. The more m/z values that are monitored, the larger the value of n and the longer it takes to acquire a mass spectrum. As more ions are monitored, the duty cycle decreases. For example, measuring 10 m/z values yields a duty cycle of less than 10%, while measuring 100 ions reduces the duty cycle to lower than 1%.

With an ITMS it is possible to simultaneously store ions over the entire mass spectrum and scan them out within milliseconds. In the ITMS the duty cycle is a function of the ion accumulation and storage time, t_{accum} , and the time to scan the ions out of the trap, t_{scan} , and is given by:

$$t_{\text{accum}} / (t_{\text{scan}} + t_{\text{accum}}).$$

The duty cycle is independent of the number of ion peaks present over the range of interest, typically m/z 30–150 for VOCs measured by a PTR-MS. The duty cycle therefore increases as accumulation time increases. For the data presented here, accumulation times were around 200 ms and scan times, with a scan rate of 12 000 Th/s, were 10 ms. This results in a duty cycle of 95%. Accumulating ions for 10 ms would only lower the duty cycle to 50%, independent of the number of protonated species present. The higher duty cycle of an ITMS also results in faster time response for the acquisition of signals for multiple species. For 10 m/z values monitored with a dwell time of 200 ms, the linear quadrupole would have a time response of 2 s, while the response for the ITMS would be 220 ms for all species in the given mass range. For fast applications such as flux measurements this can dramatically increase the amount of data that can be collected.^{25–28}

The second advantage of the ITMS over a linear quadrupole is its ability to perform MS/MS on mass-selected ions. Collision-induced dissociation (CID) can also be implemented on a standard PTR-MS instrument by increasing either the drift tube voltage, a voltage at the end of the drift tube, or a voltage at the interface with the quadrupole.¹⁴ The problem with this approach is that this does not enable isolation of the precursor ions with specified m/z of interest. The resulting CID data will exhibit fragmentation products arising from all of the ions present in the drift tube. Only in cases where one m/z value is predominant might it be possible to relate an observed fragment ion to a specific precursor ion in order to aid in compound identification. In contrast, the ITMS can isolate an ion of interest of specified m/z and collisionally dissociate the isolated ion through application of tailored waveforms or filtered noise fields (FNF).^{29–31} These methods take advantage of the fact that ions in an ITMS oscillate in ion trajectories similar to Lissajou figures, with high frequency micromotion at the RF drive frequency superimposed on a lower, mass-dependent secular frequency. Stimulation of ions of a specific m/z at this secular frequency causes excitation of ions with this m/z , and can be used to selectively eject them from the ion trap or to induce CID depending on the FNF amplitude applied. Inverting the same waveform used for isolation and using lower FNF amplitude to produce CID without ejection from the ion trap enables generation of a product ion spectrum. Thresholds for the FNF amplitude that corresponds to production of fragments depend on the duration of the FNF signal, indicating that dissociation is induced by the accumulated energy from many collisions. A comparison of single-collision fragmentation in a triple quadrupole mass spectrometer with CID by FNF for dimethylphosphonate ion showed that an FNF p-p voltage of 0.4 V applied for 20 ms corresponded to an ion kinetic energy of 10 eV in the triple quadrupole.³² Other comparisons have shown similar results.³¹ The resulting spectra can be used to differentiate between isobaric species.

This work presents key examples of MS/MS spectra of isobaric protonated species that are important in current applications of a PTR-MS. The first shows fragments with different m/z values, allowing quantitative differentiation of the two isobaric species in mixtures. A second example shows fragments with the same m/z values but different

intensity ratios. If only one species is present in the sample, unambiguous identification will be possible; if it is a mixture, only ratio estimates can be given.

EXPERIMENTAL

We have constructed a prototype instrument by interfacing a commercial hollow cathode discharge source/drift tube assembly (Ionicon, Innsbruck, Austria) to a Finnigan ITS40 ion trap mass spectrometer upgraded with Teledyne Apogee hardware and software. The Apogee upgrade provides MS/MS capability through FNF technology. The standard ion trap electron gun assembly was replaced with an interface designed to facilitate transport of ions from the drift tube to the ion trap while leaving the standard top flange of the ion trap unchanged. This was necessary to allow future use of the ITS40 instrument in its standard configuration without the external drift tube, and constrained several parameters in the interface design. A schematic of this prototype instrument is shown in Fig. 1. A simple Einzel lens system is used to focus the ions from the drift tube exit into the ITMS. This part is differentially pumped, reducing the pressure from 2 mbar (standard operating pressure in the PTR-MS) in the drift tube region to below 10^{-5} mbar in the ion trap (without helium added). The pressure in the interface is estimated to be less than 10^{-2} mbar. A lens at the end of the drift tube with 1 mm orifice and a pinhole lens with a 500 μm orifice on top of the trap provide the restrictions necessary for differential pumping and maintenance of proper operating pressures in both the drift tube and ion trap manifold.

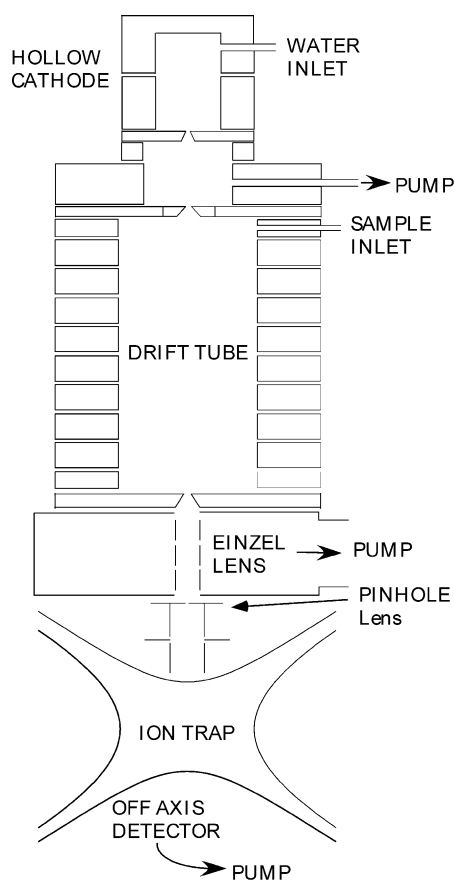


Figure 1. Schematic diagram of the PTR-ITMS.

Ions from the drift tube were pulsed into the trap by varying the potential applied to the pinhole lens, allowing it to serve as an ion gate. Ions were typically injected and stored for 200 ms. In MS/MS mode, isolation and CID times of 20 ms produced good results. The ions were ejected from the trap and detected using the standard mass-selective axial instability mode of operation³³ with scan rates of 12 000 Th/s. FNF amplitudes for isolating and ejecting the ions were in the range 4–5 V, for CID typical up to 0.5 V; all FNF amplitudes in this paper are peak-to-peak (p-p) amplitudes.

Helium was used as buffer gas as in normal ion trap operations. The best results were obtained with an ion trap pressure between 10^{-4} and 8×10^{-4} mbar (uncorrected reading of the ion gauge, sensitivity for He is 0.18). This high pressure proved necessary for removal of excess ion kinetic energy and efficient trapping of injected ions. The standard continuous dynode electron multiplier was replaced with a Burle Channeltron 4773 conversion dynode/electron multiplier assembly (Burle, Lancaster, PA, USA) to provide off-axis detection of positive ions and reduce line-of-sight noise from photons and high-energy neutrals generated in the PTR source. The lowest background signals were achieved with the conversion dynode at ground potential. In this mode the dynode acts as a 'pusher' for positive ions.

For these measurements the drift tube was operated at a pressure of 2 mbar with 500 V drift voltage, and the hollow cathode discharge was operated at 600 V with 5 mA current limitation; all other conditions were the same as in standard PTR-MS instruments.^{1,3,4} The ion trap was kept at room temperature and a pressure of 5×10^{-4} mbar. For MS/MS analyses, sample concentrations of 2–4 parts per million by volume (ppmv) were used to ensure sufficient signal levels to observe both the parent and fragment peaks in the mass spectrum. Trace gas standards were made by injecting gas samples drawn from the headspace of the pure substance of interest, at room temperature, into a 500-mL Tedlar bag (SKC Inc., PA, USA) and diluting with nitrogen or synthetic air to the desired concentration.

RESULTS AND DISCUSSION

The goal of this study was to investigate the value of coupling a PTR hollow cathode ion source/drift tube assembly to an ion trap mass spectrometer instead of a linear quadrupole mass analyzer. This investigation focused on two major questions. First, can ions be extracted from the drift tube and stored in the ion trap with sufficiently high extraction, injection, and storage efficiencies^{34–37} to achieve detection limits in the ppbv–pptv range? Second, can the MS/MS capabilities of the resulting system adequately distinguish between important isobaric species? Our approach was to build a simple interface, based on commercial instrumentation, that would allow us to determine the extraction, injection and storage efficiencies and the corresponding sensitivities. Such a functional PTR-ITMS system also allowed testing the effectiveness of MS/MS capabilities of the ITMS for resolving isobaric interferences. This system also provided several insights into potential design improvements for a next generation system.

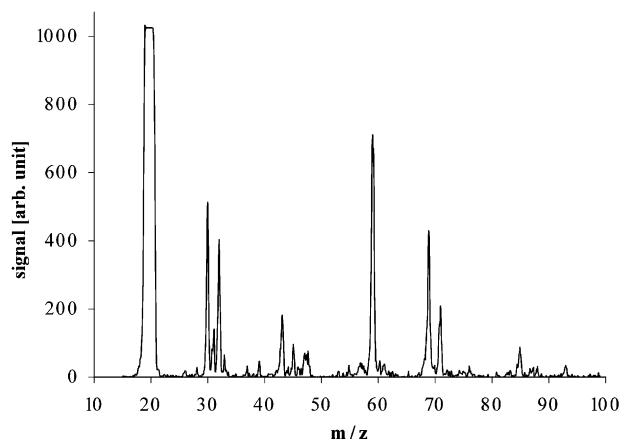


Figure 2. Ions collected in the ITMS formed via reaction between H_3O^+ and a gas mixture containing acetaldehyde (m/z 45), ethanol (m/z 47), acetone (m/z 59), isoprene (m/z 69), MVK (m/z 71) and toluene (m/z 93) in the PTR ion source. Other ions include H_3O^+ (m/z 19), NO^+ (m/z 30) and O_2^+ (m/z 32), and unidentified impurities at m/z 85, 43, and 31.

Figure 2 depicts a spectrum of ions that were produced by sampling a gas mixture, containing several organic compounds, into the PTR ion source. Following reaction with the H_3O^+ cation in the PTR ion source, reactants and products were collected and stored in the ITMS and then scanned out to produce the spectrum. The primary reagent ion H_3O^+ (m/z 19) was stored in the trap simply in order to show a complete mass spectrum. This ion is present in such high numbers that it leads to a saturation of the detector and a severe broadening of the peak, indicating that the total number of ions stored in the trap is approximately 2×10^5 . This is the number at which space charge effects become significant in a standard ITMS.³¹ Resolution and sensitivity are greatly improved during normal operation by not storing the large number of H_3O^+ ions. The next two peaks at m/z 30 and 32 correspond to NO^+ and O_2^+ respectively, two ions that are produced in the ion source in much smaller numbers than H_3O^+ .^{1,4}

The mixture measured in this case consisted of acetaldehyde, ethanol, acetone, isoprene, methyl vinyl ketone and toluene. Protonated molecules can be seen at m/z 45 for acetaldehyde, m/z 47 for ethanol, m/z 59 for acetone, m/z 69 for isoprene, m/z 71 for MVK, and m/z 93 for toluene. A peak at m/z 31 can also be seen and could be due to an impurity. However, this ion is more likely a fragment ion of acetone, which is present in high concentration and, as will be shown below, forms a fragment at this mass-to-charge ratio. The additional peaks visible at m/z 43 and 85 result from unidentified impurities. No water cluster ions such as $(\text{H}_2\text{O})_2\text{H}^+$ at m/z 37 or $(\text{H}_2\text{O})_3\text{H}^+$ at m/z 55 are observed in this spectrum. In contrast, such ions are commonly observed in spectra recorded using the commercial PTR-MS instrument and often have an intensity of around 2% of that of unclustered H_3O^+ .^{1,4} The explanation for this difference between the PTR-MS and the PTR-ITMS is that the water cluster ions undergo fragmentation before they can be detected in the latter. This can happen via CID with the helium buffer gas when the ions enter the trap, as reported recently by Kiendler *et al.*¹⁸ using an external ion flow reactor

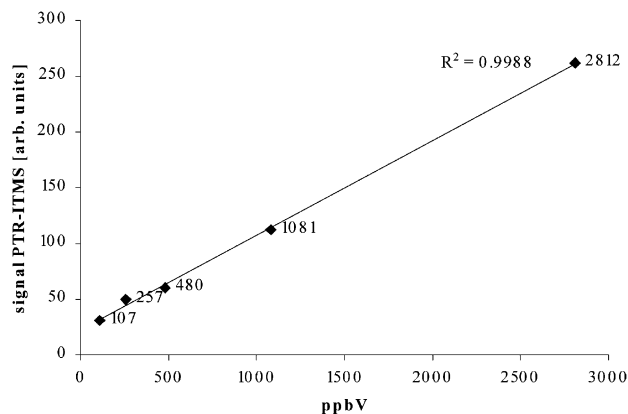


Figure 3. Calibration curve for benzene; concentrations determined using the PTR-MS along the x-axis, signal obtained using the PTR-ITMS along the y-axis.

coupled to an ion trap. It is also possible that CID was occurring in the differentially pumped interface region. In the next generation instrument, placing the extraction lens system in a chamber separated from the differentially pumped region will exclude this possibility.

Figure 3 shows a calibration curve for benzene obtained using this instrument. Samples at different concentrations were prepared by injecting different amounts of gas withdrawn from the headspace over pure benzene into a Tedlar bag filled with synthetic air. The resulting concentrations were determined by sampling bag air into a commercial PTR-MS system (Ionicon, Innsbruck, Austria), calibrated with a gas standard (Apel-Riemer Environmental, Inc., Denver, CO, USA). As shown in Fig. 3, the PTR-ITMS instrument shows a linear response in the concentration range observed. The detection limit was determined to be approximately 100 ppbv, defined as the smallest concentration detectable with a signal-to-noise ratio of 3:1.

The single most important factor limiting sensitivity in the current setup of the PTR-ITMS is noise. The same ion trap system, without an external drift tube source, has a noise level lower than 5% of that of the current system. There are two major sources for this increased background noise, namely, the high pressure in the ITMS and the location of the conversion dynode. We were constrained in mounting the detector so that part of the conversion dynode was in a direct line with the exit hole in the endcap. A vacuum chamber designed specifically for the PTR-ITMS should eliminate both sources of noise by providing differential pumping of the detector and allowing off-axis detection with no line-of-sight path for neutrals or photons. Eliminating these sources of noise would lower the detection limit by more than an order of magnitude. Additional modifications in the interface to improve pumping speed, such as an additional stage of differential pumping, will allow larger orifices to be used at the end of the drift tube and at the pinhole lens. An increase in orifice sizes by a factor of three would also provide nearly an order of magnitude improvement. Further, incorporation of a more sophisticated lens system will allow the ion beam to be focused into the ion trap and to be tuned in energy to optimize trapping efficiency while providing superior spatial focusing. Further improvements can be made to eliminate analog

noise by switching to pulse counting ion detection for the low count rates encountered when sampling low VOC concentrations. We are confident that the cumulative effects of these improvements on the prototype PTR-ITMS would result in a detection limit of 1 ppbv or lower for the second-generation instrument.

The second goal of this study was to determine how well protonated isobaric species can be distinguished by MS/MS using CID within the ion trap. One common isobaric interference generated by chemical ionization using proton transfer reactions is at m/z 71; this corresponds to either protonated methyl vinyl ketone (MVK) or methacrolein (MACR). Both are of importance in atmospheric chemistry because they are isoprene oxidation products. Using the conventional PTR-MS it is not possible to distinguish between them, but as we will demonstrate, the PTR-ITMS in MS/MS mode can differentiate between MVK and MACR.

Figure 4 shows the product ion spectra of MVK at different FNF amplitudes (Figs. 4(a)–(c)), the product ion distribution (Fig. 4(d)), and proposed fragmentation mechanism (Fig. 4(e)) for protonated MVK. The top spectrum (Fig. 4(a)) shows the isolated MVK ion measured at m/z 71. Increasing the FNF

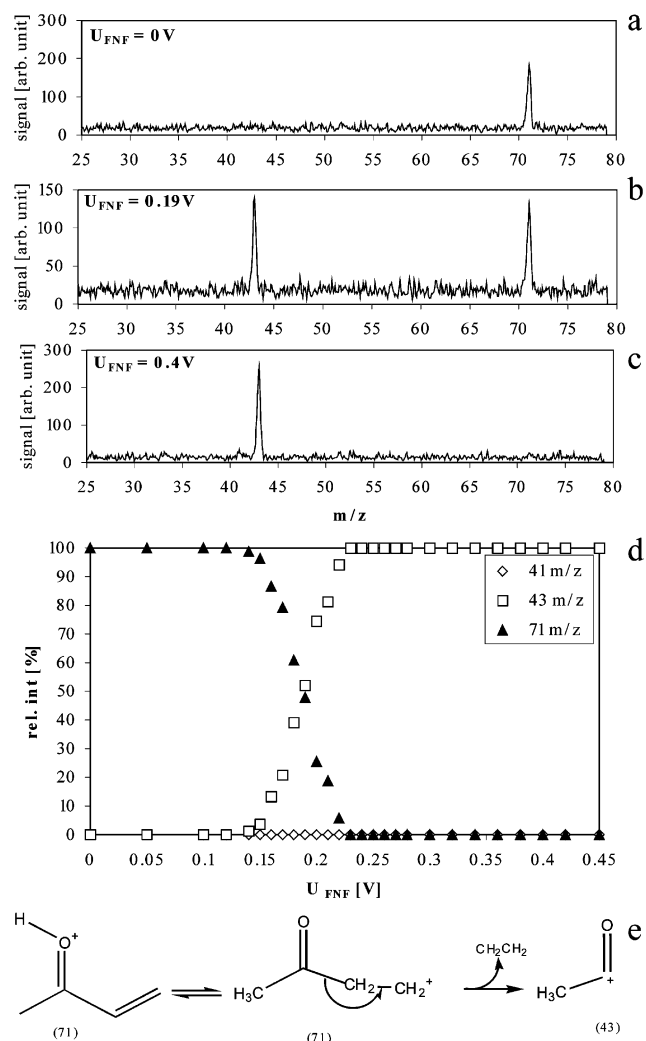


Figure 4. MS/MS of MVK: (a) isolated precursor ion; (b) fragment and precursor at $U_{\text{FNF}} = 0.19$ V; (c) $U_{\text{FNF}} = 0.4$ V; (d) product ion distribution as a function of U_{FNF} ; and (e) proposed fragmentation mechanism.

amplitude for CID gives rise to a fragment ion at m/z 43, as seen in the second spectrum (Fig. 4(b)). At higher fragmentation energy (FNF CID voltage of 0.19 V) the precursor and fragment ion intensities are approximately the same. In the next spectrum (Fig. 4(c)), where fragmentation energy has been increased further (FNF CID voltage of 0.4 V), the precursor ion is no longer visible and only the fragment ion can be observed. This figure also shows the breakdown and appearance potentials (Fig. 4(d)) of the precursor and product ions determined by increasing the FNF amplitude from 0 to 0.45 V in 27 steps. A pictorial representation of the fragmentation process is given in Fig. 4(e); for further explanation on fragmentation mechanisms the reader is referred to the literature.³⁸ Two protonated structures may be formed for MVK, with protonation at the carbonyl oxygen or at the double bond. At higher FNF voltages, the protonated molecule will lose a vinyl group to yield the acetyl fragment ion.

Figure 5 shows similar spectra for MACR. The precursor/product ion spectra are given in Figs. 5(a)–5(c), the ion intensity as a function of FNF voltage in Fig. 5(d), and a proposed fragmentation mechanism in Fig. 5(e). While only one fragment ion was observed at m/z 43 in the case of MVK (Fig. 4(b)–4(d)), fragment ions at both m/z 41 and 43 were observed for MACR (Figs. 5(b)–5(d)). The differences in the two product ion spectra therefore allow differentiation of MVK from MACR in an unknown sample. If MS/MS yields only a fragment at m/z 43, MACR can be ruled out as possible contributor to the signal at m/z 71. If at a FNF voltage of 0.4 V the relative intensities of the peaks at m/z 43 and 41 are approximately 65:35 (Fig. 5(d)), as with pure MACR, there is no interference from MVK. Otherwise, if both the fragments are present, these ratios can be used to determine the amounts of MVK and MACR in the sample. This quantitative method will only work if there are no isobaric species that produce m/z 71 other than MVK and MACR. If other contributors are likely to be present, then these interferences should be investigated as well.

A rationalization of the fragmentation process is shown in Fig. 5(e).³⁸ In the case of MACR three protonated structures may occur, showing protonation at the carbonyl oxygen or at the double bond. When protonation occurs at the C(2) atom, the acyl hydrogen can shift from the carbonyl to the C(3) atom. This may be followed by the loss of carbon monoxide to give an ion at m/z 43. The fragmentation channel leading to m/z 41 has a higher appearance potential than that for m/z 43, and increases in importance at higher collision energies. This suggests that the ion at m/z 43 undergoes sequential fragmentation at higher activation collision energy. In other words, loss of CO can be followed by a loss of H_2 , producing an ion at m/z 41.

The next pair of isobaric compounds that was evaluated was acetone and propanal. In a conventional PTR-MS instrument these species undergo proton transfer reactions with H_3O^+ and produce ions with a mass-to-charge ratio of 59. Figure 6 shows the product ion distributions obtained for both compounds by MS/MS in the PTR-ITMS instrument. Unlike the case of MVK and MACR, where fragment ions were observed at different m/z values, these two compounds both produce fragments at m/z 41 and 31. However, they do

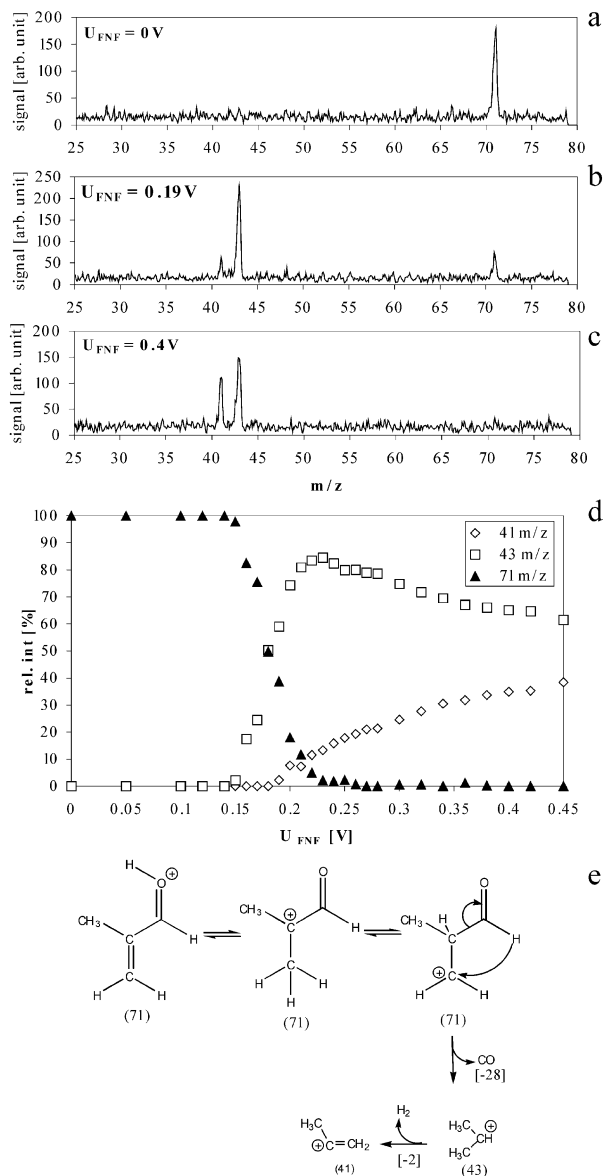


Figure 5. MS/MS of MAC: (a) isolated precursor ion; (b) fragment and precursor at $U_{FNF} = 0.19$ V; (c) $U_{FNF} = 0.4$ V; (d) product ion distribution as a function of U_{FNF} ; and (e) proposed fragmentation mechanism.

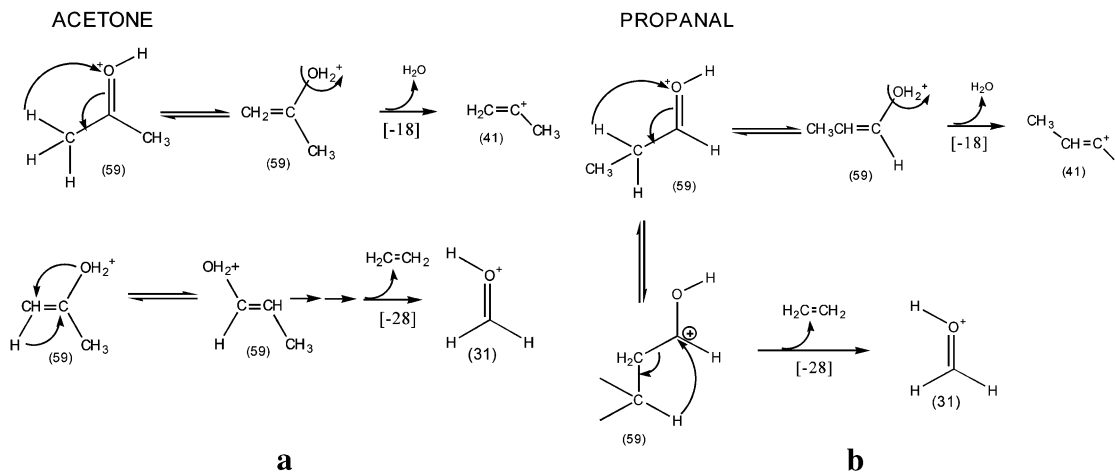


Figure 7. Fragmentation mechanisms proposed for protonated acetone (a) and propanal (b).

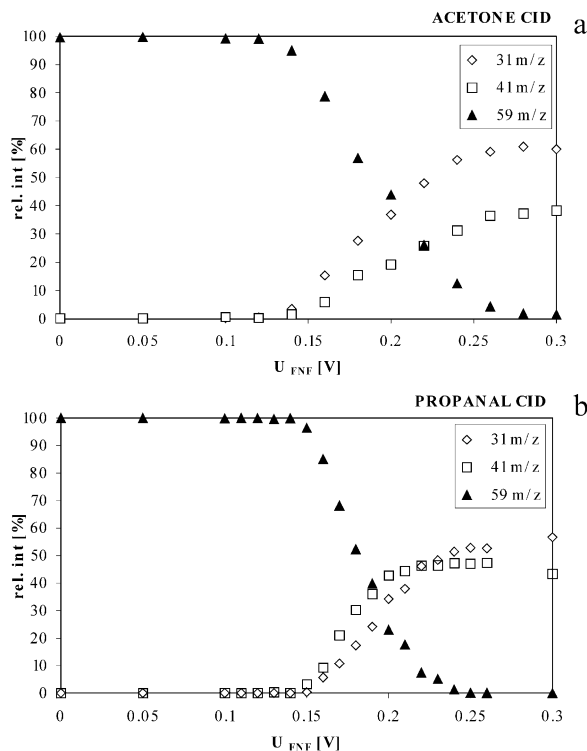


Figure 6. Product ion distribution as a function of U_{FNF} for protonated acetone (a) and propanal (b).

show slightly different abundance ratios as the FNF amplitude is increased. Fragmentation of the protonated molecule at m/z 59 seems to occur faster for propanal than for acetone. Such information may only be helpful for differentiating between these two compounds when a sample contains either 100% propanal or 100% acetone, and not a mixture of the two. Evaluating the ratios of these fragment ion intensities or the decline of m/z 59 at increasing FNF amplitudes might be helpful in deciding which of the two substances is present.

The fragmentation mechanisms proposed for protonated acetone and propanal shown in Fig. 7 illustrate this behavior.³⁸ For both acetone and propanal, protonation occurs at the carbonyl oxygen. Following rearrangement, a neutral molecule of water can be ejected to yield an ion at m/z 41. In the case of protonated propanal, a hydrogen can

migrate from C(2) to the carbonyl carbon. This ion can then lose a molecule of ethylene to yield protonated formaldehyde at m/z 31. The same fragment ion at m/z 31 is observed for acetone although this fragment ion cannot be produced directly from the protonated acetone molecule. Further rearrangement, shifting the protonated hydroxyl from C(2) to C(1) at higher energies, can result in similar formation of protonated formaldehyde at m/z 31.

CONCLUSION

The results presented here strongly suggest that further development of the PTR-ITMS will lead to a useful instrument for trace gas analysis. The PTR-ITMS has a higher duty cycle than PTR-MS instruments using linear quadrupoles. A higher duty cycle is especially valuable for measurements in environments where concentrations change rapidly and where a full spectrum is desirable. While our current detection limits are only in the 100-ppbv range, the projected detection limits of an improved second-generation system are in the low-ppbv or high-pptv range. Such detection limits will make the PTR-ITMS a useful tool for a variety of applications. We have also demonstrated that, while the MS/MS capability of the ITMS can be a helpful tool for differentiation between isobaric protonated species in some situations, it is clear that MS/MS is not a panacea. Future studies will not only investigate MS/MS to distinguish between a variety of isobaric species, but also explore the use of selective ion-molecule reactions inside the ion trap as an additional method for identifying ambiguous compounds.

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