

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/9043646>

Analysis of Volatile Organic Compounds in Air with a Micro Ion Trap Mass Analyzer

ARTICLE *in* ANALYTICAL CHEMISTRY · SEPTEMBER 2003

Impact Factor: 5.64 · DOI: 10.1021/ac034043k · Source: PubMed

CITATIONS

28

READS

19

4 AUTHORS, INCLUDING:



Peter T A Reilly

Washington State University

62 PUBLICATIONS 1,115 CITATIONS

SEE PROFILE

Analysis of Volatile Organic Compounds in Air with a Micro Ion Trap Mass Analyzer

Jeremy Moxom, Peter T. A. Reilly, William B. Whitten,* and J. Michael Ramsey

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6142

Analysis of several volatile organic compounds in air has been demonstrated with a micro ion trap mass analyzer equipped with a semipermeable membrane sampling inlet. MS/MS of selected compounds was also shown to be feasible with the miniature ion trap and could be used to improve sensitivity by reducing background noise.

Micro ion trap mass analyzers with submillimeter dimensions have been shown to operate at lower voltage and higher frequency than conventional laboratory instruments while achieving comparable spectral resolution.^{1–4} The sensitivity of these devices has not been fully explored, however. The purpose of this paper is to describe experiments with a membrane inlet for atmospheric sampling coupled to a 1-mm-diameter ion trap for analysis of volatile organic compounds. Detection limits for representative substances have been determined. We have also shown that tandem mass spectrometry can be performed for more positive identification if necessary and for background noise reduction if improved sensitivity is required.

Since mass spectrometers usually operate at pressures far below ambient, the analytical sensitivity for trace atmospheric constituents is customarily expressed as a concentration limit of detection in air at atmospheric pressure. While the instrument can obtain a measurable response from a few ions, the analytical sensitivity will depend on the sample pressure within the ionization source, ionization and transport efficiencies, and the noise of any background signal that is present. Direct expansion of the air into the vacuum chamber of the instrument can be employed⁵ and has the advantage that the sampling is relatively unbiased with respect to the molecular properties of the sample constituents. However, an appreciable quantity of air and water vapor are also admitted. Some of the sample rarification on introduction can be avoided by taking advantage of the selective permeation of certain polymer membranes that can effectively concentrate volatile organic samples with respect to the permanent atmospheric gases.

The use of semipermeable membrane sample introduction for mass-spectral analysis of trace organic compounds in air has been

widely studied in the past decade.^{6–11} Kotiaho et al. have reviewed the work prior to this period.¹² Badman et al. showed that a membrane inlet could be coupled to a miniature cylindrical ion trap for analysis of trace organics in water.¹³ Most of the recent work has been with Silastic silicone latex tubing or sheet as the membrane. Various mechanical arrangements have been used, but the most simple is to pass the sample of air at approximately atmospheric pressure through a tubular membrane with the outer surface of the membrane connected to the low-pressure mass spectrometer inlet or, as in the present case, within the ion trap vacuum chamber.

LaPack et al.¹⁴ have studied the permeation of silicone latex tubing by gases and a large number of organic compounds. They determined the diffusion coefficient, D , the Henry's law solubility coefficient, S , and their product, $P = DS$, the permeation coefficient for these substances in a tubular membrane composed of 69 wt % poly(dimethylsiloxane) and 31 wt % fumed silica, Silastic silicone latex tubing from Dow Corning Corporation. The experimental values correlated well with results of a model based on Hildebrand solubility parameters. Under conditions in which the sample concentration is negligible at the downstream side of the membrane, the steady-state flow rate, F , of sample through a tubular membrane can be written,¹⁵

$$F = 2\pi LDKC_s / \ln(r_o/r_i) \quad (1)$$

where r_o and r_i are the outer and inner radii of the tube of length L ; C_s is the sample concentration inside the tube; D , the diffusion coefficient; and K , the distribution constant between the membrane and air. K is related to the Henry's law solubility coefficient, S , by $K = Sp_T$ where p_T is the total pressure within the tubular

- (1) Kornienko, O.; Reilly, P. T. A.; Whitten, W. B.; Ramsey, J. M. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 50–53.
- (2) Kornienko, O.; Reilly, P. T. A.; Whitten, W. B.; Ramsey, J. M. *Rev. Sci. Instrum.* **1999**, *70*, 3907–3909.
- (3) Kornienko, O.; Reilly, P. T. A.; Whitten, W. B.; Ramsey, J. M. *Anal. Chem.* **2000**, *72*, 559–562.
- (4) Moxom, J.; Reilly, P. T. A.; Whitten, W. B.; Ramsey, J. M. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 755–760.
- (5) Wise, M. B.; Guerin, M. R. *Anal. Chem.* **1997**, *69*, 9, A26–A32.

- (6) Allen, T. M.; Cisper, M. E.; Hemberger, P. H.; Wilkerson, C. W., Jr. *Int. J. Mass Spectrom.* **2001**, *212*, 197–204.
- (7) Ketola, R. A.; Ojala, M.; Sorsa, H.; Kotiaho, T.; Kostianen, R. K.; *Anal. Chim. Acta* **1997**, *349*, 359–365.
- (8) Cisper, M. E.; Garrett, A. W.; Cameron, D.; Hemberger, P. H. *Anal. Chem.* **1996**, *68*, 2097–2101.
- (9) Virkki, V. T.; Ketola, A.; Ojala, M.; Kotiaho, T.; Komppa, V.; Grove, A.; Facchetti, S. *Anal. Chem.* **1995**, *67*, 1421–1425.
- (10) Lauritsen, F. R.; Gylling, S. *Anal. Chem.* **1995**, *67*, 1418–1420.
- (11) Cisper, M. E.; Gill, C. G.; Townsend, L. E.; Hemberger, P. H. *Anal. Chem.* **1995**, *67*, 1413–1417.
- (12) Kotiaho, T.; Lauritsen, F. R.; Choudhury, T. K.; Cooks, R. G.; Tsao, G. T. *Anal. Chem.* **1991**, *63* (3), A875–A883.
- (13) Badman, E. R.; Johnson, R. C.; Plass, W. R.; Cooks, R. G. *Anal. Chem.* **1998**, *70*, 4896–4901.
- (14) LaPack, M. A.; Tou, J. C.; McGuffin, V. L.; Enke, C. G. *J. Membr. Sci.* **1994**, *86*, 263–280.
- (15) LaPack, M. A.; Tou, J. C.; Enke, C. G. *Anal. Chem.* **1990**, *62*, 1265–1271.

membrane. Luo et al.¹⁶ have treated the more general case in which the sample is removed at the downstream boundary by a flow of stripping gas, giving a nonzero concentration at that boundary, and calculated the transient response to a change in input concentration.

LaPack et al.¹⁴ observed that, with the exception of strongly polar substances, such as alcohols, the diffusivities of most of the substances measured varied by less than an order of magnitude, whereas the permeabilities varied by more than three orders as a result of large differences in solubility in the polymer phase. The low diffusivity of the polar molecules was attributed to retention by the fumed silica filler.

As long as the downstream sample concentration is negligible, the sample diffusivity can be conveniently determined from the time required to reach half of the steady-state flow rate following a step change in input concentration, $t_{1/2}$ ¹⁵

$$D = 0.14(r_o - r_i)^2/t_{1/2} \quad (2)$$

The diffusion coefficient measured in this way will include the retentive effects of any filler present as well as the diffusivity within the bulk polymer.

Analytical specificity is often as important as sensitivity. The ion storage capability of ion trap mass spectrometers facilitates various forms of tandem mass analysis.¹⁷ Isolated ions can be altered by collision-induced dissociation or ion molecule reactions, and the product ions mass can be analyzed. The additional chemical information thus obtained can be used to distinguish between isomers. The techniques can also be used for background reduction and the analysis of complex mixtures. While tandem mass spectrometry has advanced to a high degree in laboratory-scale instruments, few MS/MS experiments have been tried in miniature cylindrical ion traps. For the present application of membrane-inlet mass spectrometry, the use of MS/MS for background reduction could be especially useful. As will be described below, the principal sources of background in the present experiments were vacuum pump oil residues and organic substances outgassing from the latex tubing. With MS/MS techniques, the parent ion of interest can be isolated while the background ions with masses in the spectral region of prominent fragment ions are ejected from the trap.¹⁷ After collision-induced dissociation, the fragment ions can then be detected with reduced interference in the second mass scan.

EXPERIMENTAL SECTION

The micro ion trap mass analyzer described previously^{2,4} was modified for the present work by the incorporation of a membrane inlet system for introduction of sample gases. The trap consisted of a cylindrical ring electrode with an internal diameter of 1.0 mm, separated from two planar end caps by 0.1-mm Teflon spacers. Ionization was achieved by electron bombardment from an electron gun with a Re filament. The filament was biased at -70 V, and the filament current was ~3 A, producing an electron current within the trap of ~5 μ A, measured by connecting the ring, rear endcap, and detector in parallel. The beam was gated

off by applying -100 V to the anode, which was normally grounded. The ionizing electron beam passed through the trap axially, entering and exiting through 0.3-mm holes in the end caps. Mechanical construction of the ion trap/electron gun was as described in ref 2. The trap was operated in the mass-selective instability mode by applying an 8 MHz RF voltage, with an amplitude of up to 550 V(0-p) to the ring electrode, usually with both of the end caps grounded. The trap was operated with a helium buffer gas pressure of $(2-5) \times 10^{-3}$ mbar. For the collision-induced dissociation experiments, a supplemental RF voltage was applied to one of the end caps in the form of a square wave, with an amplitude of 0.1-1 V (0 - p).

The RF voltage applied to the ring electrode was generated by a Stanford Research Systems (SRS) DS345 function generator, modulated by a second unit of the same type. This signal was amplified by an Amplifier Research 150A100A linear power amplifier, the output of which was coupled to the ion trap by a tuned step-up transformer for impedance matching. Ions were detected with a K & M Electronics, 7575MHL channel electron multiplier. A grid held at -600 V between the ion trap and the detector was used to accelerate and focus ions leaving the trap. Signals from the electron multiplier were amplified by an SRS SR570 low noise current preamplifier, and data were collected on a Tektronix TDS 420A digital oscilloscope, normally operated in a signal-averaging mode. The 1400-V bias to the detector was reduced to 1000 V during ion generation to prevent overloading the detector and preamplifier.

The membrane inlet system consisted of a 15-cm length of Silastic tubing (Dow Corning) with an i.d. of 0.51 mm and an o.d. of 0.94 mm mounted inside the vacuum chamber adjacent to the ion trap, as shown in Figure 1. The tube was attached to the ends of two hypodermic needles passing through the vacuum flange. This length of tubing was found to give an acceptable compromise between sensitivity and the amount of air admitted into the vacuum chamber. The analyte was introduced to the system by mixing a known quantity with air in a 20-L bag. The mixture was then pumped through the Silastic tube by a roughing pump at a pressure of 670 mbar with a flow rate of 5 mL min⁻¹.

In a typical MS scan, the RF voltage on the ring electrode was held constant at ~90 V(0 - p), for 50 ms, during which time the electron beam was passed through the trap, causing ions to be formed and trapped. The electron beam was then interrupted, the detector bias was increased from 1000 to 1400 V, and the RF voltage was linearly ramped to ~500 V over 20 ms. This caused ions to be ejected from the trap sequentially and recorded on the digital oscilloscope.

In the present setup, the detection limit was determined largely by the presence of background gases in the vacuum system. The base pressure, with no analyte or He buffer gas added, was $\sim 2 \times 10^{-6}$ mbar. The detection limits were found by comparing the ion signals with the noise on the background over a comparable mass range. First, a mass spectrum was obtained for a known analyte concentration. Then the background was measured 10 times, and the detection limit was defined as the analyte concentration in air that would give a signal for the most abundant species in the mass spectrum, that was equal in amplitude to twice the standard deviation of the background, integrated over the same mass range.

(16) Luo, Y. Z.; Adams, M.; Pawliszyn, J. *Anal. Chem.* **1998**, *70*, 248-254.

(17) McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J. *Int. J. Mass Spectrom. Ion Processes* **1991**, *106*, 213-235.

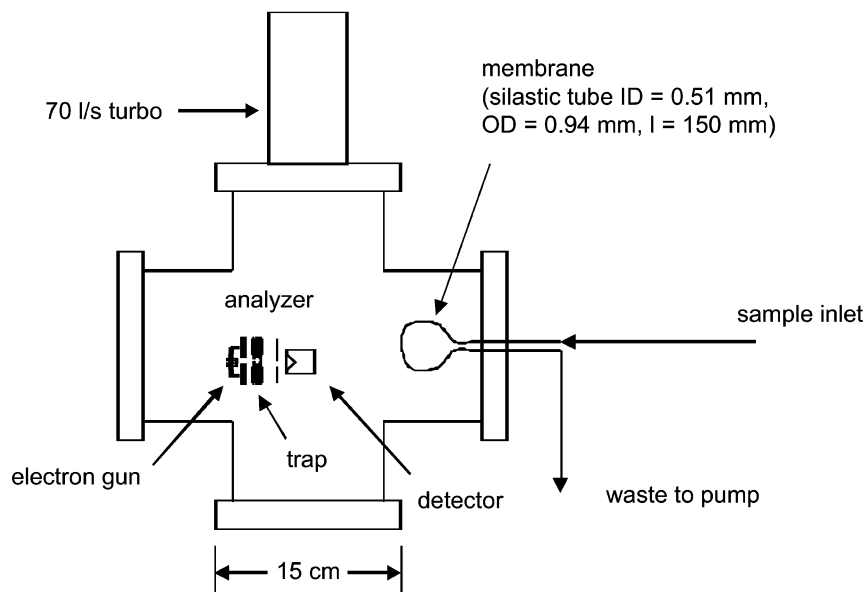


Figure 1. Vacuum chamber with membrane inlet and micro mass spectrometer electrodes, electron gun, and detector.

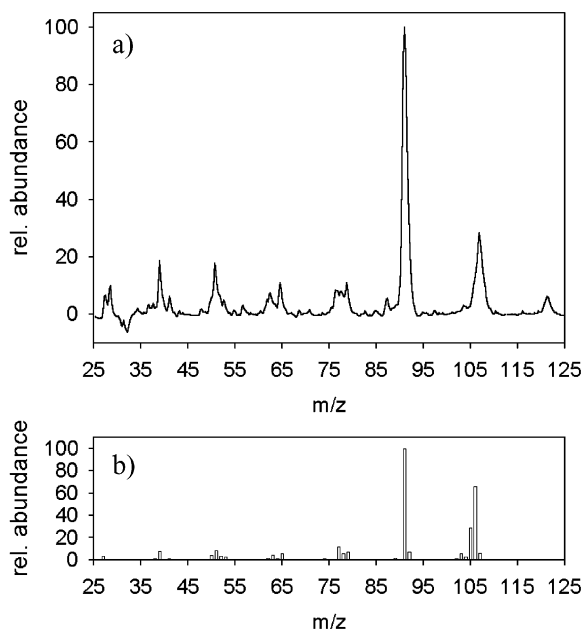


Figure 2. (a) Mass spectrum of 100 ppm xylene in air and (b) mass spectrum of xylene from ref 18.

The time response of the membrane inlet system was determined by measuring the intensity of the ion signal as a function of time after opening the valve to allow the analyte through the membrane tube. This was done for a variety of samples, including polar and nonpolar molecules and xenon. In each case, the signal increased with time and saturates as expected. The sample was then removed from the inlet line, and air was pumped through to measure the decay or purge time of the system. All of the measurements were made at room temperature.

RESULTS AND DISCUSSION

A mass spectrum of xylene at a concentration of 100 ppm in air is shown in Figure 2 compared with the 70-eV electron impact mass spectrum from the NIST Standard Reference Database.¹⁸ The spectrum was averaged over 100 scans. The background has

Table 1. Limits of Detection of Selected Volatile Organic Compounds

substance	limit of detection (ppm)
acetone	13.8
benzene	0.32
dichloroethane	1.32
DMMP	7.40
toluene	0.54
xylene	0.26

been subtracted from the experimental spectrum. Some evidence of ion molecule reactions between the fragment ions and neutral parent molecule can be seen at mass 122. This mass is larger than the parent ion mass and probably consists of the parent plus an additional methyl group. Collisions between the trapped ions and neutral molecules within the trap caused a reduction in signal at higher sample concentrations.¹⁹

A mass spectrum of dimethylmethylphosphonate (DMMP), averaged over 100 scans, is shown in Figure 3. This compound is sometimes used as a surrogate for organophosphate chemical weapons agents. As we shall show below, ion-molecule reactions were observed between some of the fragment ions and parent molecules, with the parent being ionized by charge exchange with the fragment ions.

Detection limits for the various organic compounds studied are summarized in Table 1, expressed as molar fraction. There was a wide range in calculated detection limits, with the best sensitivity for the volatile aromatic compounds. The background signal appeared to be largely due to aliphatic hydrocarbons, probably from vacuum pump oil or substances outgassing from the latex tubing. The noise limiting the sensitivity was mostly due to fluctuations in the background rather than instrumental noise, so detection limits better than those shown in Table 1 should be achievable with a cleaner vacuum system. The response time also

(18) NIST Standard Reference Database 69; November 1998 Release: NIST Chemistry WebBook.

(19) Dawson, P. H.; Lambert, C. J. *Vac. Sci. Technol.* **1975**, *12*, 941–942.

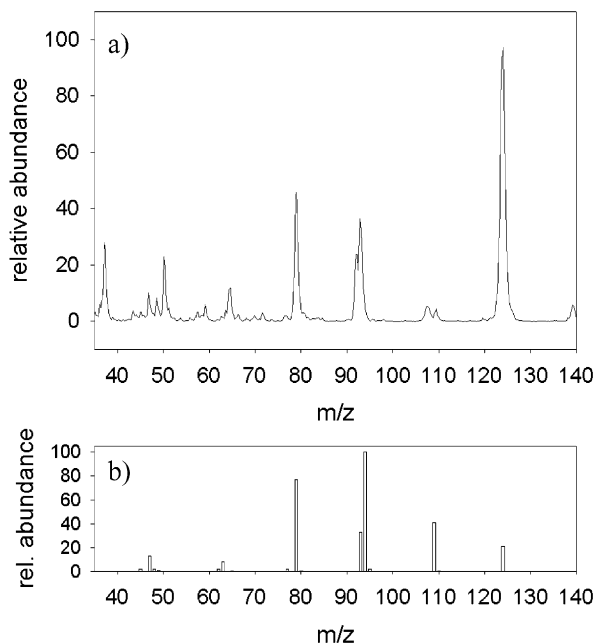


Figure 3. (a) Mass spectrum of dimethyl methylphosphonate and (b) mass spectrum of dimethyl methylphosphonate from ref 18.

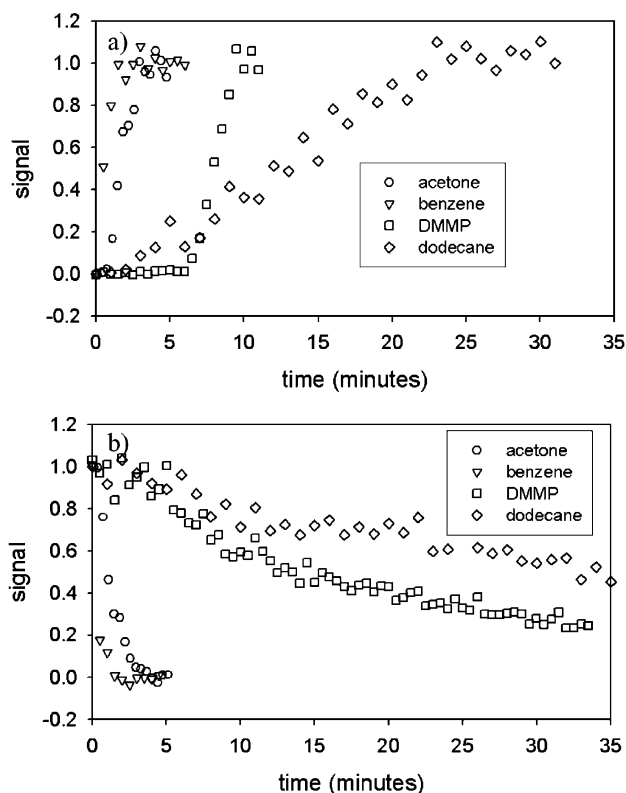


Figure 4. Time dependence of largest mass spectral peak for various analytes: (a) rise time and (b) fall time.

varied considerably for different substances, as shown in Figure 4 where the temporal responses for acetone, 2-propanol, benzene, and DMMP are displayed. The aromatic compounds showed a more rapid response, as compared to dodecane. DMMP exhibited a more unusual time dependence that may be due to adsorption of DMMP by the fumed-silica filler present in the latex tubing.¹³

We have been able to perform tandem mass spectrometry in the micro ion trap in essentially the same manner as is routinely

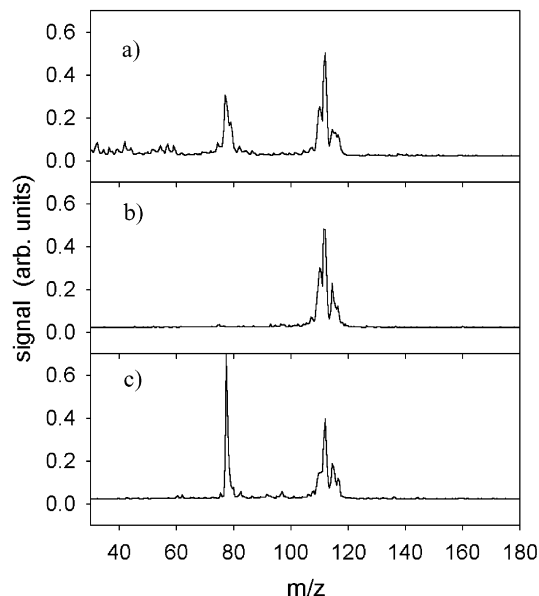


Figure 5. (a) Normal mass scan of chlorobenzene, (b) isolation of parent ions, and (c) spectrum after collision-induced dissociation.

done in conventional traps.¹⁷ Tandem mass spectrometry was performed by first ionizing the molecule and then isolating and fragmenting the parent molecular ion. The fragmentation was accomplished by applying a supplemental RF signal to one of the end caps to increase the kinetic energy of the ions, inducing dissociation by collisions with the He buffer gas. Fragments thus produced were trapped and then mass-analyzed by ramping the RF amplitude on the ring electrode. The supplementary voltage was turned off during the mass scan. MS/MS results with chlorobenzene are presented in Figure 5. The mass spectrum in Figure 5a clearly shows the parent ions at m/z 112 and 114 and the benzene fragment at m/z 77. Most of the ion peaks at lower m/z values were due to the residual background of hydrocarbons, probably due to pump oil and outgassing from the membrane. Isolation of the parent ion by increasing the ring electrode voltage is demonstrated in Figure 5b. A supplementary voltage applied to one of the endcap electrodes was not in resonance with the parent ion secular frequency during ion storage or ejection. The results of collision-induced dissociation are shown in Figure 5c. After isolation, the voltage on the ring electrode was reduced until the benzene fragment ion was stable in the trap and the secular frequency of the parent ion was resonant with the supplemental endcap voltage.¹⁷ Under these conditions, the benzene fragment reappeared at m/z 77 as a result of dissociation of the parent molecular ion.

One practical advantage of using the MS/MS technique is the improvement in the signal-to-noise ratio obtained in our spectrometer. Most of the observed noise is due to fluctuations in the background signal in the mass region of the measured peak. In the MS/MS process for chlorobenzene, the background signal around m/z 77 was significantly reduced, resulting in an improved signal-to-noise ratio for the m/z 77 ion obtained via MS/MS, as compared to that obtained with the parent ion using simple MS. Although only a portion of the background signal was random noise and in this case the isolated fragment ion had a lower integrated intensity than the parent ion peaks, the detection limit was still improved by a factor of 2.1.

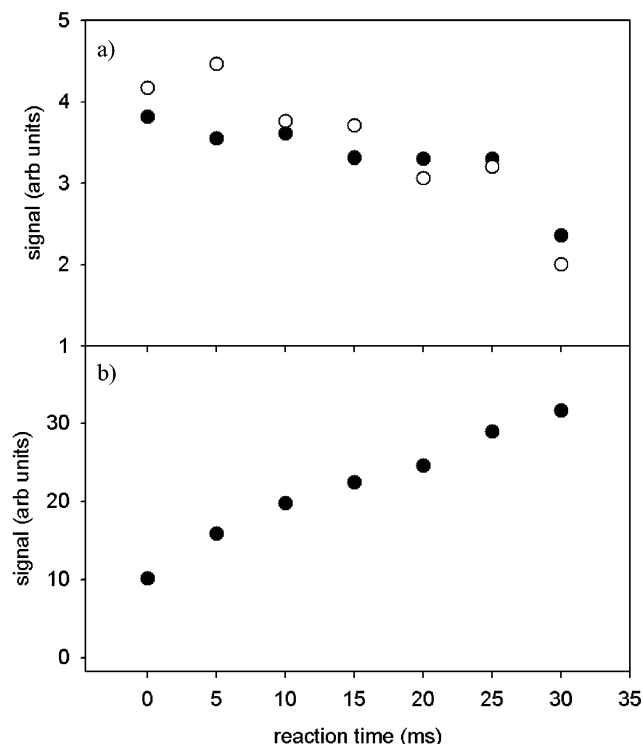


Figure 6. Charge exchange MS/MS of dimethyl methylphosphonate: (a) decay of fragment ions; open, m/z 94; solid, m/z 79; and (b) growth of parent ion.

With substances in which the fragment ions have a higher ionization potential than the parent molecule, it is possible to observe a different form of tandem mass spectrometry in which isolated fragment ions ionize neutral molecules within the trap.

We show in Figure 6 the time dependence of the growth of the DMMP parent ion as a result of charge exchange with the previously isolated fragment ions at m/z 79 and 94. Such a process might be useful for increasing the specificity of trace detection of organic phosphates.

We have shown in the present investigation that volatile organic substances in air can be analyzed with a miniature ion trap mass analyzer with detection limits somewhat poorer than those of conventional instruments. Substantial improvements are anticipated if the background gas signal can be reduced, since fluctuations in background signal are the major source of noise. Another hindrance to detection in the present trap configuration is the short interaction length within the trap for electron impact ionization. More efficient ionization should yield a significant reduction in sample pressure to achieve the same signal intensity. Although at this stage only the mass analyzer has been miniaturized, small vacuum pumps of the required speed are becoming commercially available, and the electronics are relatively simple and amenable to miniaturization. Thus, the achievement of a hand-portable environmental mass spectrometer appears to be presently feasible.

ACKNOWLEDGMENT

This research was sponsored by the U.S. Department of Energy, National Nuclear Security Administration, Office of Nonproliferation Research and Engineering. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

Received for review January 16, 2003. Accepted May 2, 2003.

AC034043K