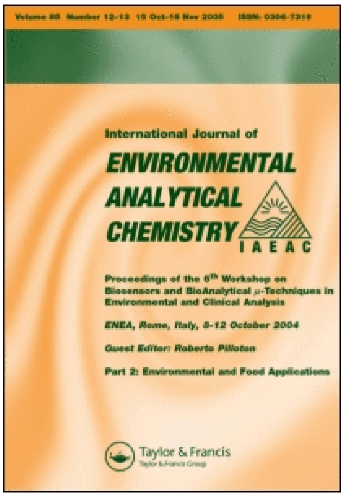

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Monitoring of Airborne Organic Vapors Using Ion Mobility Spectrometry

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To cite this Article Eiceman, G. A. , Snyder, A. P. and Blyth, D. A.(1990) 'Monitoring of Airborne Organic Vapors Using Ion Mobility Spectrometry', International Journal of Environmental Analytical Chemistry, 38: 3, 415 — 425

To link to this Article: DOI: 10.1080/03067319008026945

URL: http://dx.doi.org/10.1080/03067319008026945

Intern. J. Environ. Anal. Chem., Vol. 38, pp. 415–425
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MONITORING OF AIRBORNE ORGANIC VAPORS USING ION MOBILITY SPECTROMETRY

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(*Received 12 June 1989; and in final form 10 August 1989*)

Automated, continuous monitoring of organic vapors in air under three field designs for plume drift was demonstrated using a hand-held ion mobility spectrometer (IMS) in characterizing IMS behavior as a point sensor. In one field study, the IMS was placed 50 cm from a 9 m^2 grass plot contaminated with methylsalicylate and response to airborne vapors was recorded during a 13 hr period of atmospheric turbulence to illustrate susceptibility of point sensors to wind direction. A similar study under near-quiescent atmospheric conditions was made using dimethylsulfoxide. In a third study, the plume from a point source of dipropyleneglycolmonomethylether was interrogated over a 25 m × 12 m grid downwind with windspeeds of 6–18 km h^{-1}. Laboratory studies were used to measure instrumental response times and influences from potentially interfering atmospheric organic pollutants.

KEY WORDS: Air monitoring, organic vapors, ion mobility spectrometry.

INTRODUCTION

The need for continuous monitoring of airborne hazardous organic vapors in certain industrial situations is presently undisputed though sensing technologies are still somewhat imperfect. Electrochemical detectors are susceptible to ageing and instability during air monitoring while optical spectroscopies are susceptible to interferences from particulate matter and non-chemical atmospheric phenomena. Several promising technologies for air monitoring are based on gentle ionization of gaseous contaminants and include a range of sophistication from modified electron capture detectors[1] to atmospheric pressure chemical ionization-mass spectrometers (APCI-MS). Continuous and rapid analysis of ambient air by APCI-MS was demonstrated during the release of pesticides in greenhouses[2,3] and

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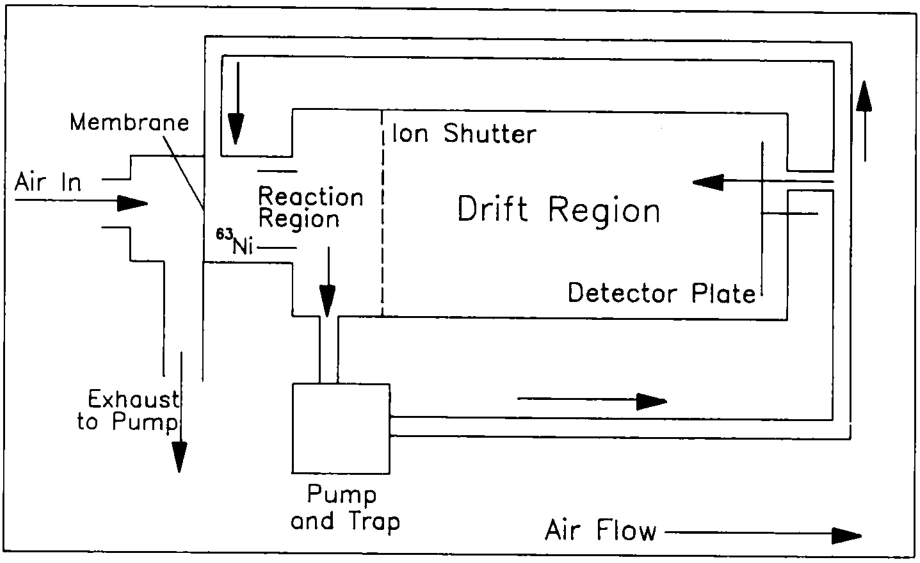

Figure 1 Schematic of hand-held Ion Mobility Spectrometer with membrane inlet.

with industrial emissions in urban areas.[4] Such capabilities could be employed in chemical tracer studies, industrial perimeter monitoring, and combustion stack analysis, but routine applications of APCI-MS are compromised by instrumental complexity and expense. In contrast, inexpensive sensors such as electron capture detectors are unreliable for analysis of mixtures. Positioned between ECDs and APCI-MS in performance, cost and complexity is ion mobility spectrometry which affords detection limits similar to ECDs with further characterization of samples through gaseous ionic mobilities.

Ion mobility spectrometry (IMS) is a simple instrumental technique in which airborne vapors are drawn into a reaction region (Figure 1) and the analyte is converted to product ions with a radioactive ^{63}Ni ion source.[5] Product ions are separated using differences in gaseous mobilities which are largely governed by the ionic collisional cross-sections.[6] Separations in IMS are a function of ion size rather than mass as in mass spectrometry and mobility differences impart a second dimension of selectivity to IMS analyses apart from the ionization preferences. All processes in IMS occur in air at ambient pressure so instrumentation can be hand-held and relatively inexpensive. Although IMS had been suggested for air monitoring previously, actual environmental investigations with IMS have been limited in number and scope. Watson and Kohler[7] compared the detection of airborne nickel carbonyl by IMS with infrared spectrometry and Dam[8] measured eight hour concentration emission profiles of an unnamed toxic pollutant from an industrial point source. Blyth[9] reported the profiling of vapor plumes using several ionization devices including a hand-held IMS suitable for continuous air monitoring. Despite these developments, IMS has not been actively exploited as a tool for atmospheric environmental monitoring perhaps due to early reports on perceived inadequacies.[10] These problems seem to be due more to the particulars of atmospheric pressure chemical ionization than to deficiencies in resolution by ionic mobilities.

The initial IMS event of analyte ionization is based on electron or proton exchanges between a reservoir of reactant ions in the ion source and the analyte of interest. Due to the large collisional frequencies of ions and molecules at atmospheric pressure, ionization is competitive and ionization efficiency depends upon both capture kinetics and concentrations of neutral analytes. An exact quantitative description of IMS response with mixtures is under theoretical and practical development[11] and only approximate predictive models currently exist. Thus, to successfully apply IMS in airborne vapor monitoring, the analyte of interest should be considerably greater in proton or electron affinities than potential interferents. When target vapors have medium or low proton or electron affinities, interferences can occur and are evident in the mobility spectrum. In such instances, product ions may be formed through alternate ionization strategies including photoionization.[12] However, compounds with low or medium affinities for proton or electrons can register strong responses in IMS so long as molecules with stronger affinities are absent during the analyses.

Ion mobility spectrometry has largely been considered a laboratory tool and only recently have hand-held wholly portable instruments become available for use in atmospheric monitoring.[13,14] One objective for the present work was to examine the response characteristics of a hand-held IMS with respect to quality of mobility spectra, response times, and memory effects. The objective for the field component of our study was to illustrate the capabilities of IMS for airborne vapor monitoring as well as the limitations inherent with all point sensors. All studies were completed with compounds that serve as non-toxic nerve agent simulants and which should also be characteristic of pesticides and several other important industrial materials.

EXPERIMENTAL

Instrumentation

An ion mobility spectrometer from Graseby Analytical Limited (Watford, UK) was equipped with a 3 cm drift region, 10 mCi ^{63}Ni ion source, 1 cm reaction region, and dimethylsilicone membrane inlet and is available as model AVM (Figure 1). The IMS was operated at ambient temperature and pressure with purified air as the carrier and drift gas. Signals were processed using a Graseby Analytical ASP board/software designed specifically for use in an IBM PC/XT/AT compatible microcomputer for automated continuous sensing by IMS. Other operating conditions were: ion shutter pulse width, 300 ms; frequency of analysis, 13 Hz; and drift region field of 210 V cm^{-1}. A Hewlett-Packard (HP) model 3390A recording integrator was connected to the ASP board analog output and operated at 3 cm min^{-1}.

In laboratory studies, a flow tube was constructed of 8 cm diameter × 1.5 m long rigid PVC pipe and laboratory air doped with organic vapors were delivered through the tube to the IMS using a model 4600X System Paps fan (Pamotor, Burlingame, CA). The IMS was placed in the flow tube cross section at the opposite end of the pipe and air flow was roughly $6 \times 10^3 \, m^3 \, s^{-1}$ or $0.3 \, m \, s^{-1}$. In field studies, the IBM-PC/AT was placed in a hatchback compact automobile and was used on site in a spacious grassland at the Edgewood Area, Aberdeen Proving Grounds. The site was equipped with line power and a portable meteorological station, model EWS (Climatronics Corp., Bohemia, NY), for continuous recording of temperature, dew point, wind speed, and wind direction.

Procedures

Laboratory Studies-Known volumes (5–10 uL) of organic compounds were applied as neat liquid to a tissue placed 1 cm from the flow tube fan and mobility spectra were continuously recorded at an interval of 8 s between acquisition and storage of spectra (64 scans averaged per spectrum). Plumes of 10–90 s were generated by removing the vapor source, after the appropriate delay, from the drift tube fan. Compounds obtained from Aldrich Chemical Co. (Milwaukee, WI) were dimethylsulfoxide (DMSO), dipropyleneglycolmonomethylether (DPM), triethylphosphate (TEP) and methylsalicylate (MSAL). The estimated concentrations of these vapors in the flow tube at steady state were estimated as $0.5\text{–}1 \, mg \, m^{-3}$. In interference studies, a steady-state concentration of individual vapors was generated and 200 uL of interference were added to a second tissue located next to the vapor source yielding pulses of $1.1 \, g \, m^{-3}$ for interference vapors. Interferents were selected to represent a broad range of compound classes or proton affinities and included hexane, benzene, methylene chloride, methanol, and ammonia. Interferents were obtained in reagent grade quality from various commercial sources.

Field Studies-The effect of wind direction on IMS sensing was measured from 4:30 PM (May 16, 1988) to 6:00 AM (May 17) during a tornado watch in eastern Maryland when a violent storm moved easterly from 4–8 PM. Strong winds moved in direction from the north and east (0–90 °) and then from the south and east (90–180 °) as the storm front passed near the test site. A 3 m × 3 m square plot of grass (with the longitudinal edges aligned to magnetic north) was sprayed with 50 mL of a fine mist of 40% MSAL in peanut oil (by volume). This oil was added to reduce the effective vapor pressure of MSAL. The IMS was placed 3 cm from ground level at a distance of 50 cm initially downwind from the NW corner of the square. Spectra were recorded continuously at 4 min intervals (2000 scans per spectrum) for 13.5 hrs. Environmental conditions were: wind speed, $0\text{–}48 \, km \, h^{-1}$; wind direction, 0–270 °; and air temperature, 15–22 °C.

In a second study, a point source of DPM was used to generate a plume, and mobility spectra were obtained at 0, 2.5, 5, 10, 15, 20, and 25 m distances downwind from the source, at elevations of 1 to 2 m from the ground along 2.5–5 m intervals that were perpendicular to the plume axis. The point source was a 32 cm × 28 cm sheet of tissue paper saturated with 20 mL of DPM and was mounted on a wood frame. In addition, a vertical profile was obtained at 1 meter from the source at elevations from 10–190 cm. Environmental conditions were:

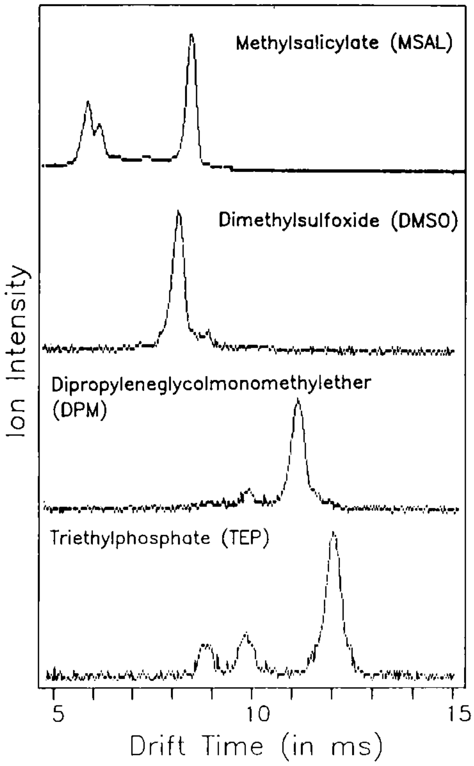

Figure 2 Mobility spectra for target vapors used in laboratory and field studies. Reduced mobilities and identities are given in the text.

wind speed, 8–16 km h^{-1}; wind direction, 220–290 °; and air temperature, 23 °C. In a final study, neat DMSO was applied to a grass plot during a period of sunny, warm weather with stable wind speed and direction. The IMS was positioned 1 m downwind from the plot and 10 cm from ground level. Spectra were recorded continuously and automatically for 5 hours from 1 to 6 PM using 1000 scans per spectrum at a 2 min interval. Environmental conditions were: wind speed, 5–8 km h^{-1}; wind direction, 270 °; air temperature, 20–22 °C.

RESULTS AND DISCUSSION

Laboratory Studies

Mobility spectra from the IMS response to positive ions for DMSO, DPM, and TEP and negative ions for MSAL are shown in Figure 2 where drift times were 8.51, 8.21, 11.1, and 12.1 ms for MSAL, DMSO, DPM, and TEP, respectively. Peak widths were 0.8–1 ms at baseline and the mobility spectra were typical of the chemical simplicity which results from soft ionization of molecules in air at atmospheric pressure in IMS. Laboratory grade IMS instruments produce com-

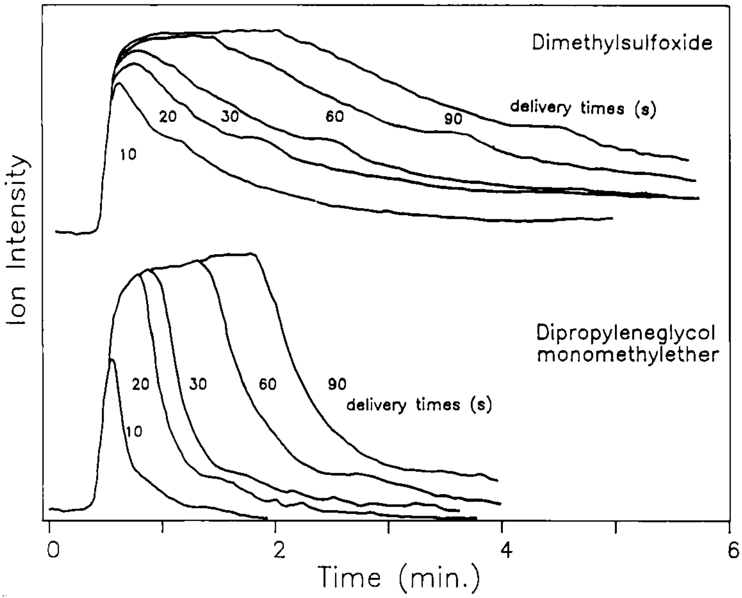

Figure 3 Ion intensities of product ions for DMSO and DPM from plumes of various duration generated for characterization of response/clearance times. The plumes were generated by exposing the flow tube to the vapor source for times of 10, 20, 30, 60, and 90 s as designated for each curve.

parable spectra with slightly narrower peak widths of 0.3–0.6 ms at baseline.[15] Product ions created in air at ambient temperature were identified with an IMS-mass spectrometer as the oxygen-monomer adduct, $M * O_2^-$, for MSAL and dimer ions, M_2H^+, for DMSO, DPM, and TEP.[16] At low concentrations for TEP and DPM, dimer ions were replaced by monomer ions, MH^+ with drift times of 9.7 and 9.8 ms, respectively. These four substances were deemed suitable as test materials for atmospheric environmental studies using IMS detection and were free of secondary complicating ion processes such as drift region fragmentation or cluster-formation.[17,18] The hand-held IMS showed moderately fast response (better than 8 s) and the stability of ion intensity, measured from 10 replicate spectra of reactant ions, was 0.9 mV standard deviation or 0.3% relative standard deviation for peak height. Limits of detection were not determined quantitatively but were estimated as $0.01\,\mathrm{mg\,m^{-3}}$. Linear ranges were about 1.5–2 orders of magnitude after which the IMS response became level.

Ion intensity profiles for 10–90 s deliveries of vapors to the laboratory flow tube are shown in Figure 3 for DMSO and DPM. The rising slopes for the plumes were virtually superimposable indicating that rates of IMS response to the vapors were independent of concentration on the time scale in Figure 3. Moreover, the curves revealed that a steady-state concentration in the flow tube was achieved only after vapor delivery of more than 60 s and corresponded to near saturation of the IMS. The time for saturation was influenced by the air flow and tube dimensions and was likely the result of transport-limited diffusion across the flow tube (under near laminar flow conditions) rather than hysteresis in the IMS. On the trailing edge of the plume, product ion intensity decreased and reactant ion intensity was restored over about a 1 minute delay for DPM at all delivery times. In contrast, DMSO product ion intensity persisted from 2–8 minutes or more and was dependent upon dosage time. Exact relative contributions to memory effects from the flow tube surfaces versus that inside the IMS could not be discerned from these results but suggest that gross overloading with certain compounds can disable IMS response through saturation of the ionization region. Recovery for the longest delivery of DPM was about 4 minutes to full restoration of reactant ions. Measurements on clearance rates of IMS alone were not made but severe exposures produced complete saturation from 20–60 s suggesting that the long recovery times were substantially influenced by vapor adsorption on the flow tube. The present IMS source configuration and tube parameters were not designed for high speed response (or rapid clearance) and these results certainly do not establish a lower limit on IMS response times. Alternate flow configurations in the ion source region may result in response times of roughly 50 ms and ultimate response times will be governed in IMS more by fluid dynamics of air sampling than by ion chemistry or electronics. The implications from response times of 1–10 s or memory effects of 10–30 s are insignificant in field studies discussed below since mobility spectra in the field studies were collected over a 2–4 min interval by signal averaging.

The target compounds chosen all had large proton or electron affinities and IMS response with these compounds should not be measurably affected by other urban pollutants including some which are also toxicologically significant. The stability of the product ion intensities during delivery of interferents at concentrations 1000–2000X greater than the analyte (which are greater levels than those likely to be found in ambient air) is shown in Figure 4. A slight decrease ($<10\%$) in product ion peak height was observed for DPM, DMSO, and TEP when ammonia was added to the flow tube. Other potential interferents added at 30 s intervals when present with the target compounds showed no detectable influence on the product ion intensity. The detection of these target vapors with this hand-held IMS in field studies will be unaffected by these potential airborne interferents.

Field Studies

Results from air monitoring near a section of grass contaminated with MSAL are shown in Figure 5 where product ion intensities and wind direction/speed have been aligned. During this monitoring episode, fluctuations in wind direction from a storm front dramatically affected IMS response to MSAL vapors from the grass plot. The effect of having placed the IMS north and west of the grass plot (inset) was a MSAL product ion intensity that was highly susceptible to slight changes in wind direction (0 to 90°) as observed from 4:30 to 9:00 PM. A strong response to MSAL was observed when the IMS was downwind of the grass plot but the intensity fell as the wind came from the south (180°). This should not be especially remarkable except that the IMS was within 50 cm of the contaminated grass and

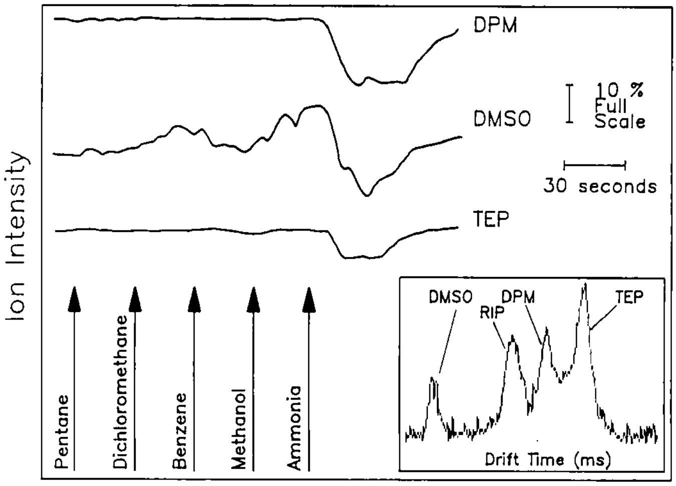

Figure 4 Plots of ion intensities for DPM, DMSO, and TEP during addition of various potential chemical interferents. The inset shows the resolution of the mobility spectra for a mixture of all target vapors and reactant ion peak (RIP).

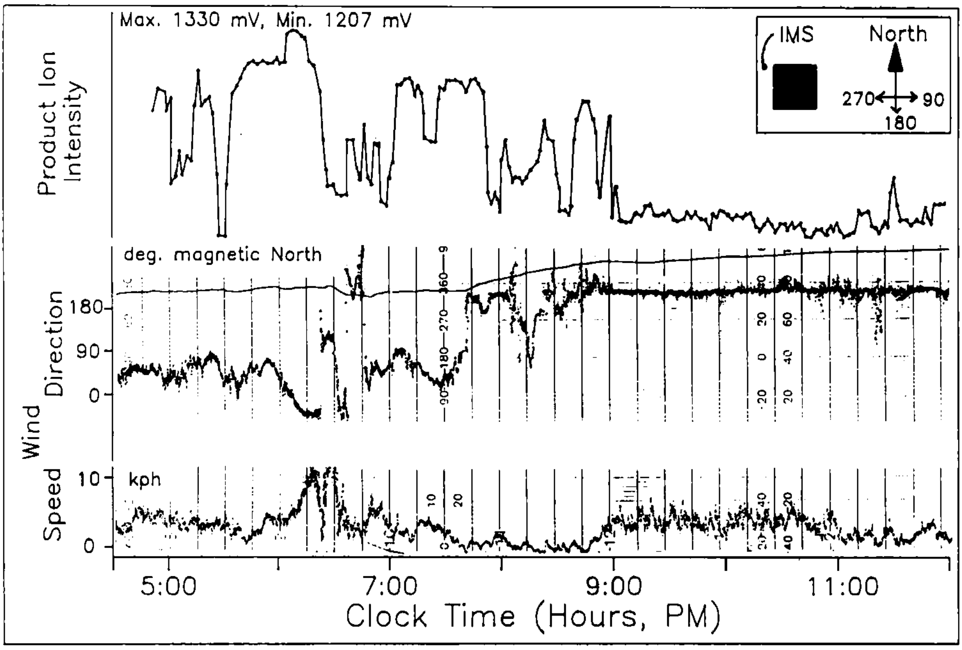

Figure 5 Product ion intensities from continuous IMS sensing near a square plot of grass contaminated with MSAL. Wind direction and speed profiles from the portable meteorological station are shown below the IMS response profile. Monitoring time was from 5 to 12 PM.

registered no response when MSAL vapors were directed away from the IMS by slight shifts in wind direction. A change in wind direction at 9:00 PM to a near constant flow from the south directed the vapor plume away from the IMS and the product ion profile from 11 PM to 6 AM showed low intensity with occasional signal spikes of 4–16 min from short-lived turbulence. These findings demonstrated both the suitability of IMS for remote unattended continuous air monitoring and the vulnerability of point sensors to changes in wind direction. During a sunny, warm day with a constant slight wind, DMSO on grass yielded saturated IMS response for 2.5 hrs and product ion intensity thereafter decayed only 40% during the next 2 hrs. Stability of response for DMSO intensity was measured at the beginning of the study when vapor concentrations were constant over a short period with a standard deviation of 21 mV and a relative standard deviation of 7.5%. Small fluctuations were removed by averaging 1000 scans per spectrum, leaving only variations caused by wind direction and speed. Under these circumstances which represent relatively calm wind conditions, atmospheric turbulence caused signal fluctuations that were 20X greater than what was observed under controlled laboratory conditions.

In a third environmental study, DPM was released continuously from a point source of vapors and the plume was evaluated downwind by moving the IMS through a region anticipated to contain DPM vapors. The results are displayed as isoconcentration contours in Figure 6 where a narrow curved region of high DPM concentration was surrounded by larger regions of lower concentrations. Since only one IMS was available and 35 positions were chosen for measurement of product ion intensity, the resolution of information about the plume was limited. Consequently, only an approximate geometry for the plume was possible with straight lines connecting measurement positions. Resolution could be improved either by recording spectra continuously as the IMS is swept through the plume region or better still by using more than one IMS in the experiment. A third option of greater number of sampling points was disqualified due to unacceptably long delays from analysis times of 2 min per position. This analysis time was comparatively long but was considered necessary to signal average the response due to fluctuations in wind direction and expected shifts in plume position over the sampling grid. Neither of the former options was available for the present study and resolution was fixed at 2 m increments for the width and 5 m increments for the length.

The plume was also interrogated at 2 m in elevation (not shown) from ground where DPM was virtually undetected. This finding was preliminary evidence that the plume was not dispersed equally in all directions and suggested that the organic vapor sank toward the ground and was dispersed. When the IMS was brought to a distance of 1 m from the source, movement of vapor toward the ground became evident as shown in a concentration-elevation profile (inset) immediately downwind of the source. The implications of turbulence from a nearby shelter and poor spatial resolution render these data unsuitable for matching to plume models. However, these results illustrate the suitability of IMS as a chemical monitor for comparable or related investigations. In that regard, IMS was stable, convenient, and highly automated and permitted time-resolution

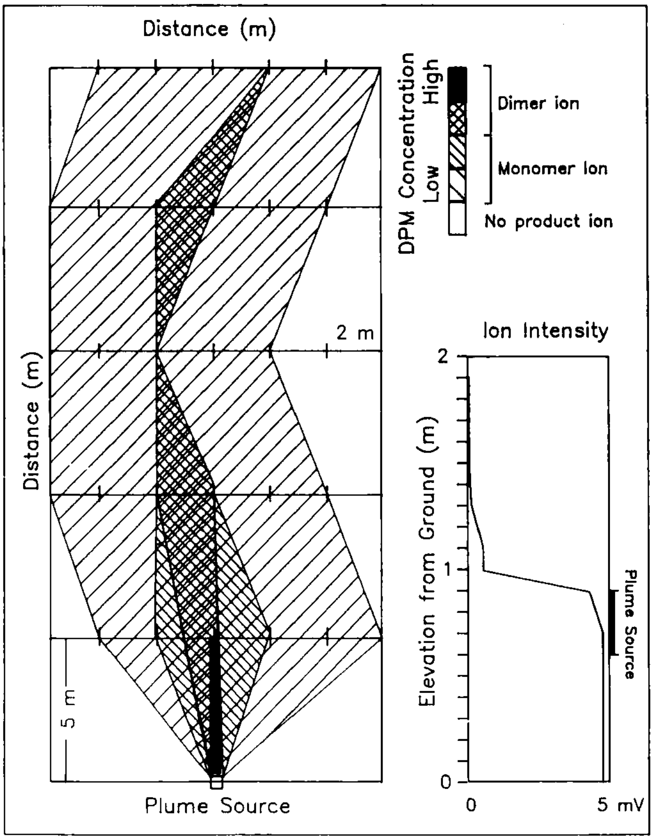

Figure 6 Estimated isoconcentration contours from IMS sensing at 1 m from ground. The point source was located approximately 1 m from ground level. The inset shows the vertical concentration profile 1 m downwind from the point source.

of plume fluctuations on the 3–10 s time scale. Long-term stability in response and calibration drift in IMS will be explored in future investigations.

CONCLUSIONS

Ion mobility spectrometry exhibits dynamic response to organic vapor plumes with response times better than 8 seconds in a commercial configuration. Memory effects may be compound related and if excessive can render the IMS unresponsive. Potential atmospheric pollutants with lower proton/electron affinities exhibited negligible effects on IMS response against the target vapors at concentrations 1000–2000X larger than those for the analyte. Environmental applications of IMS for continuous air sensing near contaminated earth demonstrated both the suitability of IMS for unattended operation with advanced signal processing and the susceptibility of point sensors to fluctuation in wind direction. Plume characterization from a point source was also demonstrated but the utilization of several IMS devices would dramatically enhance both the speed and spatial resolution of plume mapping.

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