HAND-HELD GC-ION MOBILITY SPECTROMETRY FOR ON-SITE ANALYSIS OF COMPLEX ORGANIC MIXTURES IN AIR OR VAPORS OVER WASTE SITES

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ABSTRACT

Ion mobility spectrometry (IMS) was formally introduced approximately 21 years ago, and has been used as a detector for chemical warfare agents. IMS research and development outside the military has recently been the subject of renewed interest. Military IMS units are small, rugged, and portable which makes them ideal candidates for inclusion in portable airborne vapor monitoring systems. The strengths of IMS are low detection limits, a wide range of application, and simplicity of design and operation. The gentle ionization processes used in IMS impart a measure of selectivity to its response. However, atmospheric pressure chemical ionization with compounds of comparable proton affinities leads to mobility spectra for which interpretive and predictive models do not exist. An alternative approach for the analysis of complex mixtures with IMS is the use of a separation device such as a gas chromatograph (GC) as an inlet. The attractions of GC-IMS over GC-mass spectrometry (MS) for field use include the small size, low weight, and low power demands of GC-IMS.

Parameters in GC-IMS which required examination before further development or field application included three major concerns. The first was selection of an optimum temperature of the IMS detector and evaluation of the effect of IMS temperature on mobility spectra. The second was a study of the stability and reproducibility of chromatographic retention and mobility behavior. The final issue was the

development of suitable data reduction methods. Results suggest that an IMS cell temperature of ca. 150° to 175°C provided mobility spectra with suitable spectral detail without the complications of ion-molecule clusters or fragmentation. A commercially available, portable IMS unit was configured as a GC detector to evaluate the possibility of using the unmodified unit as the basis for a portable prototype. Significant fluctuation in peak heights were observed (ca. +/- 12%), but mobilities varied slightly (ca. 1 %) over a 30 day test period. Neural network pattern identification techniques were applied to data obtained at room temperature and at 150°C. Results showed that spectral variability within compound classes was insufficient to distinguish related compounds when mobility data was obtained using the commercial room temperature IMS cell. Similar but less severe difficulty was encountered using the 150°C data. Incorporation of retention indices as a referee parameter was useful in eliminating false positives.

INTRODUCTION

Background

The detection of trace levels of hazardous organic volatile compounds in complex mixtures represents an analytical and sampling challenge. Waste site sampling requires ppb detection limits in samples comprised of complex matrices and mixtures of from ten to hundreds of analytes. Other considerations include the time of sampling and time of analyses, delays in analysis, labor costs, labor training, and cost/sample ratio. The time and expense of complete laboratory analyses can force that fewer samples be taken with the attending risks. Technical aspects make the translation of widely accepted laboratory instrumentation (GC-MS and GC-FTIR) difficult or unsatisfactory due to cost and complexity. Certainly, gas chromatography with some advanced detector will be required for chemical resolution of complex mixtures of organic compounds over waste sites. Proven detectors such as mass spectrometry and infrared spectrometry allow necessary specificity of detection but represent cumbersome and intricate instrumentation not easily configured for field use. These instruments often require highly skilled operators as well. The high power consumption of portable GC/MS and GC/IR systems certainly limits their use in many field situations. Other detectors which have been

common to portable GC units lack specificity and necessitate a reversion to dual column or dual detector methods for confirmation of peak assignments. The development of a hand-held GC-IMS combines the separation power of GC in combination with a multidimensional detector. The release of the civilian counterpart of the military IMS units was a logical starting point for development of a portable GC-IMS.

Ion Mobility Spectrometry

Ion mobility spectrometry (Figure 1) is based on the ionization of vapors in air at atmospheric pressure. The differentiation of ions occurs by measurement of gaseous ionic mobilities (1). A typical IMS instrument is divided into two regions. The first is the reaction region containing an ion source (typically ^{63}Ni). Ion separation occurs in the second (drift) region of the spectrometer, where separation is based on the size-to-charge ratio of the ions. The ion shutter that separates the two regions injects ions from the reaction to the drift region using period pulses of the shutter field. The drifting ions are detected at the end of the drift tube by a detector plate.

In IMS, ionization occurs through collisional charge transfer between a reservoir of charge, i.e. the reactant ions, and neutral analytes, M. The most abundant reactant ions generated from a beta-emitting source in air are $(H_2O)_n*H^+$ and $(H_2O)_n*O_2^-$. These ionic clusters co-exist at near thermal energies in the reaction region. Product ions experience little or no fragmentation and exist commonly as M^+ and MH^+ or M^- and $M*O_2^-$ depending on proton or electron affinities of the neutral species. Ions formed in the reaction region are injected into the drift region by the ion shutter. In the drift region, ions move at particular drift times (t_d) through an electric field, E, of ca. 200 V/cm. For a drift region with a given length, L (cm), the drift time is related to velocity (v_d, cm/s) and ion mobility (K, $cm^2/V*s$)) through equations 1 and 2:

$$v_d = L / t_d \quad (1)$$

$$K = v_d / E \quad (2)$$

Ions strike a flat plate detector and a mobility spectrum or plot of detector current (in pA or nA) versus t_d (usually in ms) is produced. Consequently, the basis for selectivity in IMS is differences in drift times for ions governed by ion mobilities. Drift times are dependent on temperature and pressure and are normalized to reduced mobility constants, K_o, that are related to molecular

properties through the Mason-Shamp equation. In general, the equations for mobility constants are considered well-established for small spherical ions but extrapolations to large organic molecules may be tenuous. Practically speaking, direct quantitative predictions of K_o values for organic molecules are presently impossible. Mobilities are inversely proportional to collisional cross sections. Thus, IMS is an ion separator based on size/charge rather than mass/charge as found in mass spectrometers.

Ion mobility spectrometry offers advantages such as low power, simple and rugged construction, ppb detection limits, and mobility spectra representative of individual constituents. Disadvantages traditionally ascribed to IMS include significant memory effects, irreproducible behavior and complex response to mixtures (2). These difficulties can be circumvented with the addition of a GC as an inlet and with the reconfiguration of the drift tube (3,4). Furthermore, hand-held IMS instruments are currently available in military-hardened form with battery operation (5). The military IMS cells are attractive for use in portable GC units and were used as a starting point for the study of GC/IMS parameters.

Objectives

Several areas of GC-IMS have not been addressed and must be understood for practical advances in field applications of GC/IMS. The first area is optimization (or influence) of IMS temperature on GC/IMS performance and on the mobility spectra obtained from the IMS. Second is the evaluation of the effect of concentration on reduced mobility and mobility patterns. Third is the evaluation of a commercially available portable IMS as a GC detector, and the final area is the preparation of a suitable software peak identification program. Each of these has served as the basis for an objective in the work described below.

RESULTS AND DISCUSSION

Effects of Temperature on Ion Mobility

The successful development of a portable GC-IMS requires that the optimum IMS temperature be determined. This data had to be determined empirically, since little foundational theory was available. Typically, low temperature mobility behavior shows considerable ion clustering and complexity, while higher temperatures encourage ion

fragmentations. An intensive study was undertaken to determine the optimum operating temperature for the IMS since a wide variety of analytes are expected to be encountered. A representative set of 43 compounds was selected from seven different chemical classes, shown in Table 1. The temperature effect study was conducted on a Tandem Ion Mobility Spectrometer (TIMS, PCP Inc., West Palm Beach, Fla.) which allowed heating of the inlet and drift tube. Confirmational mass spectral studies were conducted on an MMS-160 IMS/MS (PCP, Inc., West Palm Beach, Fla).

There are four basic processes that can occur when a compound is introduced into the IMS. First, there may be no detectable reaction, such as when a species that is active only under positive polarity is introduced into an IMS operating in negative polarity. Second, clusters may form between the analyte and various ions such as H_3O^+, N_2^+, or NH_4^+. Such clusters appear as peaks in the spectrum. The third possibility is the formation of cluster ions which subsequently undergo equilibria reactions while in the drift tube. The magnitude of the equilibrium constant will determine the effect on the resulting mobility spectrum. If the equilibrium is slow relative to transit time, no significant effects will be seen. If the equilibrium is fast relative to the transit time, the ions arriving at the detector can differ significantly from the original ions produced, and peak broadening may result. Finally, fragmentation may occur, and the resulting spectra may exhibit such behaviors as a generalized increase in the baseline or a series or numerous small peaks. The exact manifestation will depend on the degree of fragmentation. The IMS portion of a portable GC/IMS should operate isothermally to reduce power consumption and complexity. It is thus essential to select the cell temperature such that clearly resolved, sharp, and reproducible peaks are produced. Peak broadening and fragmentation patterns will be difficult, if not impossible, for a data reduction system to classify. It is also desirable that the cell operating temperature be as low as possible to minimize power requirements. The other factor that must be considered for temperature selection is memory effect. Higher temperatures encourage rapid clearing of the cell and promote cleaner operation. Thus, 3 factors must be balanced in selecting the optimum IMS temperature: clearing time, mobility behavior, and power requirements.

The effect of IMS cell temperature on mobility behavior was studied by analyzing the 43 target compounds using nine different cell temperatures from 50 to 250°C. The results showed that while all compounds behaved differently, a general pattern was discernable. At the lower temperatures (ca. 50 to 150°C), many compounds experienced drift tube reactions, and peaks were either very broad or moved as the concentration in the drift tube changed. At the midrange temperatures (ca. 100-200°C), drift tube equilibria decreased, and stable ion/molecule clusters were observed. At the higher temperatures (ca. 200-250°C), fragmentation became prevalent. Figures 2 and 3 show two examples of compound classes and their behavior over the temperature range studied. The aromatics (figure 3) are not dramatically affected by temperature changes, although benzene and ethylbenzene do show evidence of drift tube reactions at 75 through 150°C. The alcohols (figure 4) show greater variability with temperature than the aromatics, but the general pattern of drift tube reactions-clustering-fragmentation is evident in the ethanol and n-propanol.

Members of the chemical classes of ketones, alcohols, halocarbons, and esters were examined by IMS/MS at three temperatures to confirm the data obtained using the TIMS. At 50°C, ion cluster formation dominated mobility spectra and the formation of dimer and solvated ions was evident. At elevated temperatures (150° and 225°C), these ions were not observed or present at low levels. At 225°C, fragmentation was prevalent rendering mobility spectra less informative than those from lower temperatures.

Compilation of the TIMS and IMS/MS data leads to several observations cogent to the design of a hand-held GC/IMS. First, a portable GC/IMS will require the use of a heated IMS cell to obtain distinctive and informative mobility spectra. If the instrument is to be used as a monitor for a wide range of compounds, the optimum temperature range appears to be 150-200°C. Second, the cell temperature can be set to optimize the response of selected compound classes. For example, the halocarbons showed greater spectral detail at higher temperatures than did the rest of the target compounds. If the GC/IMS is to be used as an in-situ monitor for halocarbons, the IMS cell temperature could be set at 225°C. Finally, the variations in behaviors with temperature might be useful as an added discriminator in GC/IMS applications. For

example, acetone and isopropanol have similar chromatographic retention indices on many GC columns. At lower IMS cell temperatures, isopropanol and acetone both exhibit drift tube equilibrium reactions, and their spectra have many similar features that might confuse pattern recognition software. At 175°, the spectrum of isopropanol begins to show distinct stable peaks, while acetone still shows drift tube reactions up to ca. 225°. Thus, the selection of cell temperature could be used to help discriminate between these two compounds.

Stability and Reproducibility of IMS

Graseby Analytical (United Kingdom), manufactures a portable IMS that is used by western military establishments for detection of chemical warfare agents. This IMS (abbreviated as AVM for airborne vapor monitor) was coupled to a GC to evaluate three parameters. The GC used was a Hewlett-Packard (Palo Alto, CA) 5730 equipped with a Supelco (Supelco Park, PA) SPB-5 30 meter capillary column. Nitrogen was used as the carrier gas, and makeup gas was air. The AVM operated in a water chemistry mode. The effect of concentration on mobility behavior was examined first to determine if IMS mobility patterns were significantly influenced by analyte concentration. The stability and reproducibility of the IMS response over an extended period was evaluated as well. These findings were then used to determine if it would be practical to use an essentially unaltered AVM as the IMS cell for a portable prototype GC-IMS. These findings were also used to isolate and identify those features of the AVM that could be modified to improve its performance as a GC detector.

The effect of concentration on mobility was studied by injecting a series of dilutions of each of the target compounds into the GC-AVM. Review of the data obtained led to several unanticipated findings. First, the AVM spectra of many of the positive mode compounds were very similar. The data obtained at 50°C using the TIMS did not show these similarities. As the concentration of the target analyte decreased, the similarities between the spectra generally increased. Product ions were often shoulders off the reactant ion peak as opposed to the separate product peaks usually observed using the TIMS. Finally, a clear linear relationship between peak height and concentration was not obtained over the concentration range studied. As a result, no definitive statement

regarding the effect of concentration on mobility was possible.

The reproducibility of AVM was evaluated over a 1 month period. Peak heights, drift times, and mobilities were monitored for positive and negative background spectra. The spectra of known amounts of positive and negative mode standard compounds (ethylbenzene and CCl_4, respectively) were also examined. The results of the study are shown in Table 2. The variability of intensity of the reactant and product ions showed drift over the 30 days, but reduced mobilities varied slightly. Any attempt at quantitation using only mobility spectra patterns and relative abundances would be difficult using the AVM as configured. Table 2 also shows that the larger ions exhibit more reproducible behavior, as shown by the decrease in relative standard deviations with decreases in mobility. This fact was exploited in neural network pattern identification studies which followed.

Evaluation of Neural Networks for Identification of Compounds

Neural networks have in the last 10 years become very popular for pattern recognition in many disciplines. A network consists of a series of interconnected nodes (called neurons or perceptrons) in which mathematical weighting, summation, and submission to a function are performed. The output of each neuron is then sent on to another neuron where a similar operation takes place. The network itself can consist of a variable number of neurons in a layer, and variable numbers of layers. The network is trained by submitting to it target vectors consisting of input and the target output desired. In this work, the factors included in the training vector were retention index and mobility peak data. The target output was the name of the compound possessing these GC-IMS characteristics. The network takes each training vector and adjusts the weights applied in each neuron to get the correct value output. The next training vector is submitted using the previously obtained weighting factors, and the resultant error is used to adjust the weights again. This repetitive process continues until the weights are adjusted so each training vector submitted to the network yields the correct output. Training sets may consist of hundreds of facts, and the training process itself may take hours. Once the network is trained, however, response is rapid. For this reason, neural networks are well suited for use in a portable instrument.

For this study, neural networks were used with both the TIMS data (150°C) and the AVM data. The training vectors consisted of retention indices, reduced mobilities, and in some cases, the percent relative abundance of the mobility peaks. Aspects of network structure, training, and failures were examined with both data sets. The network was unable to train on the AVM data for the alcohols. Many of the alcohol spectra were very similar, and the network was unable to distinguish between them even with the retention index included. The network was able to train successfully using the TIMS alcohol data. The difficulty with the AVM data may arise from operating the cell at ambient temperature and from using a membrane in the inlet.

A network was trained using data from all the positive mode compounds obtained at 150°C. Approximately 10% of the initial test data was set aside as a test set. The network was trained using the remaining 90% of the original data set. The trained network was able to identify ca. 95% of the test set. Failures were associated with similar compounds, i.e., within compound classes. A typical problem was differentiating ethylbenzene from the xylenes. This problem was successfully addressed by using the retention index of the test compound to determine the correct identification. For example, if the network yielded both ethylbenzene and o-xylene as potential identifications, the retention index of the test compound was compared to the retention index of the standard target compounds. In all cases of multiple identifications, this approach eliminated the false positives. In no instances were false identifications seen across compound classes, i.e., never was a ketone mistakenly identified as an alcohol when the retention index criteria was used.

CONCLUSIONS

The findings demonstrate that GC-IMS is a viable field monitoring technique, and holds promise of evolving into a genuinely portable and powerful field screening device. Elevated temperature cells, operating without membranes, will be required for such devices. Commercial portable IMS units such as the AVM cannot, as currently configured, be used as detectors for GC-IMS. While these devices work well for specialized applications, use of the AVM as a generalized detector is not possible without modifications. Neural networks can be successfully used to identify compounds when

chromatographic data is included in the training process and mobility data obtained at elevated temperatures is used. When the pattern recognition process fails to identify a compound, retention index can be used to obtain the correct identification. Neural networks are system specific. The network can not be trained using data obtained on different GC-IMS system. Aspects of the chromatographic and mobility behavior (via temperature) can be modified to suit specific applications or can be set to cover a broad range of target compounds. The small size and low power requirements of GC-IMS combined with the ability to tune the instruments to different applications gives GC-IMS an advantage over many other portable techniques.

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Table I. Listing of analytes studied using GC-IMS.

Positive Mode

ALCOHOLS
- Methanol
- Ethanol
- n-Propanol
- i-Propanol
- n-Butanol
- i-Butanol
- s-Butanol
- t-Butanol

AROMATICS
- Benzene
- Toluene
- Ethylbenzene
- o-Xylene
- m-Xylene
- p-Xylene
- Styrene

ESTERS
- Methyl Methanoate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Ethyl Methanoate
- Ethyl Ethanoate

KETONES
- Acetone
- 2-Butanone
- 3-Metyl-2-Butanone
- 2-Pentanone
- 3-Pentanone

ALDEHYDES
- Propanal
- Butanal
- 3-Methylbutanal
- Pentanal
- Hexanal

Negative Mode

HALOCARBONS
- Methylene Chloride
- Chloroform
- Carbon Tetrachloride
- Trichloroethene
- 1,1,1-Trichloroethane
- Tetrachloroethene
- 1,2-Dichloroethane
- 1,1,2,2-Tetrachloroethane

CHLORINATED AROMATICS
- Chlorobenzene
- o-Dichlorobenzene
- 2-Chlorotoluene

Table 2
AVM Reproducibility Study

Description	Mean*	Rel. Std. Dev. (%)
Reactant Ions		
Peak Height		
Positive Mode	6911	11.2
Negative Mode	2109	22.2
Reduced Mobility		
Positive Mode	1.87	2.01
Negative Mode	1.60	2.18
Product Ions**		
Peak Height		
Positive Mode	935	8.65
Positive Mode	679	8.22
Negative Mode	1687	8.77
Reduced Mobility		
Positive Mode	1.64	1.19
Positive Mode	1.39	0.98
Negative Mode	2.22	0.99

*: Mobilities reported in $cm^2\ V^{-1}\ s^{-1}$ and peak heights reported in millivolts.

**: Ethylbenzene had 2 product ions.

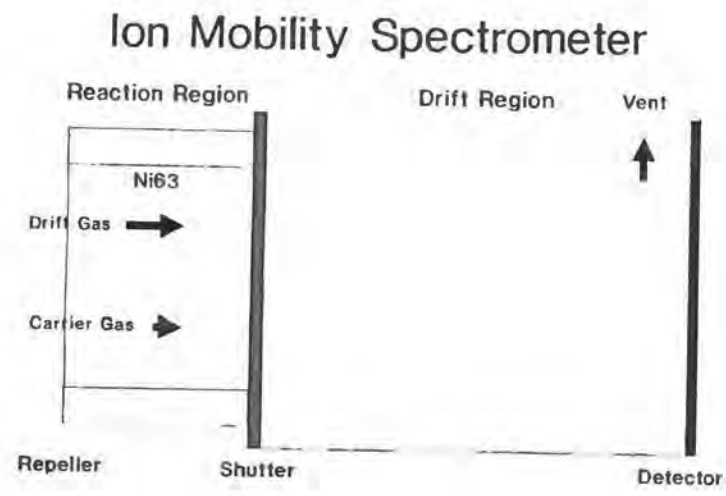

Figure 1. Schematic of ion mobility spectrometer

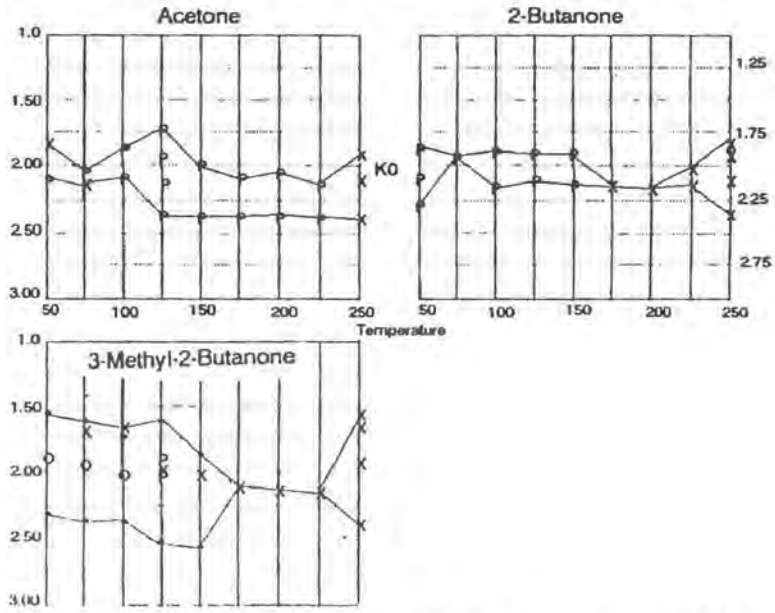

Figure 2. Behavior of selected ketones over the 9 temperatures studied. Legend for Figures 2 and 3: P: Peak that moved over the course of the elution. The P marks the extremes of the mobility. X: Distinct stable peak. *: Extremes of a drift tube reaction broadened peak. O: Approximate center of the peak associated with a drift tube reaction.

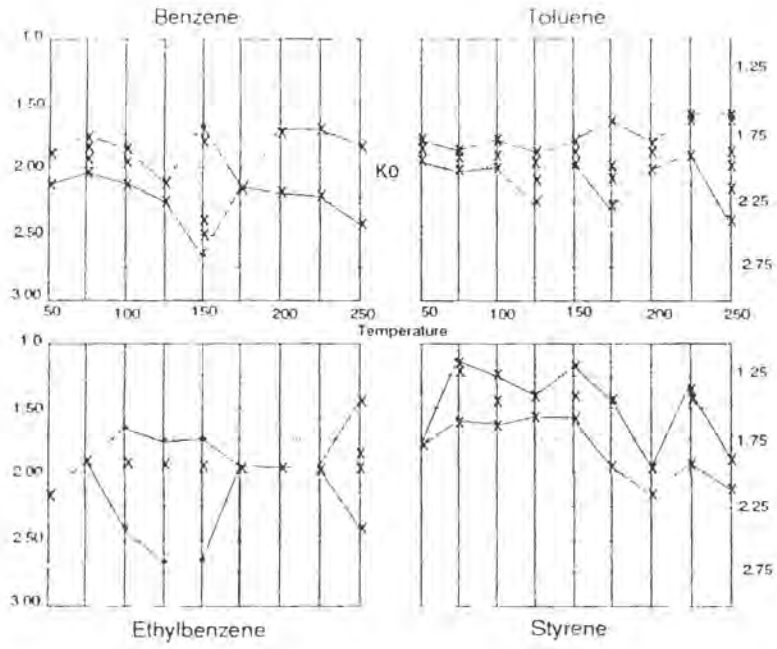

Figure 3. Behavior of selected aromatics over the 9 temperatures studied. See figure 2 for key.

DISCUSSION

COLLEEN PETULLO: Did you use the same IMS in the IMS-MS study or were several used?

SUZANNE BELL: The IMS-MS instrument was different than the heated instrument we used in New Mexico State. That's simply because we didn't have an IMS-MS available, so we simply used one that PCP was gracious to rent us for a week.

COLLEEN PETULLO: But you only used one in the study at any given time, right?

SUZANNE BELL: Right. The nine temperatures and 43 compounds were all run on one instrument. The IMS-MS was on another instrument, and then the GC-IMS was yet another instrument.

COLLEEN PETULLO: How long would it have taken you to train the neural networks if you would have programmed it for the 43 compounds?

SUZANNE BELL: I would assume it would take eight to ten hours, at the worst. The training time gets longer as you get more and more similar data. If we gave it, for example, 25 examples of benzene spectra over a wide concentration range, that would let the network generalize but you pay the price in training time. It could take hours or weeks to train the computer.

COLLEEN PETULLO: You had mentioned that you didn't do this because of time constraints.

SUZANNE BELL: Right.

COLLEEN PETULLO: How many did you ultimately program?

SUZANNE BELL: We ultimately trained 23 in the combined data set. This was about half.

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