DATA ANALYSIS TECHNIQUES FOR ION MOBILITY SPECTROMETRY

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ABSTRACT

The past several years have seen the advance of ion mobility spectrometry (IMS) as an analytical technique. Most of these advances have been made in the hardware development end of the problem, the result being that portable IMS devices have begun to appear in the marketplace. The other end of the problem, the signal processing and data analysis techniques, has not been addressed to the same degree. Recent attempts at applying data analysis techniques to IMS data have been made, and the results are encouraging. Data processing algorithms ranging from those which perform simple tasks to those performing more difficult tasks have been developed. Among the algorithms which will be discussed are algorithms for measuring the peak areas of selected peaks of interest in biological studies, and linear discriminant analysis for detecting and identifying industrial chemicals at, or near their maximum exposure limits.

INTRODUCTION

When dealing with environmental issues, there are two points of emphasis that must be considered. These two points of emphasis are the protection of individuals in the workplace, a task regulated by the Occupational Safety and Health administration (OSHA), and the protection of the environment in which we live, a task regulated by the Environmental Protection Agency (EPA). These two points of emphasis, while dealing with the same general problem, are typically at different ends of the concentration range of chemical or biological contamination or exposure. The concentration ranges for which one must monitor an individuals exposure to chemical and biological contaminants is usually in the low parts-per-million, ppm, range to tens of thousands of ppm [1-3], and is set by Federal law [3]. The concentration range which is monitored for environmental compliance is usually parts-per-billion, ppb, to low ppm. A useful method for the monitoring both concentration ranges at the same time is ion mobility spectrometry, IMS.

Ion mobility spectrometry is based upon the flow, or drift, of molecular ions through a gas of uniform temperature and pressure. A weak electric field is uniformly applied to the gas in the drift region of the IMS, causing the ions to move along the field lines. These ions continue to drift until their movement is impeded by collisions with neutral gas molecules. Since the electric field is still being applied to the gas,

the ions are accelerated once again and the process of acceleration and collision is repeated until the ions strike the detector. IMS is similar to Time of Flight mass spectrometry in that the electric field causes the ions to drift, but it differs in that Time of Flight mass spectrometry is performed under vacuum and there are few, if any collisions to retard the ions. The average velocity, v_d, of the ions is determined by millions of the accelerations and energy-losing collisions. The time required for an ion to traverse a known distance in the drift region of the spectrometer is the drift time, t_d.

The average velocity of the ions, also called the drift velocity, is related to the strength of the applied electric field through the equation

$$v_d = l_d / t_d = KE \qquad (1)$$

where v_d is the drift velocity, l_d is the length of the drift region of the spectrometer, t_d is the drift time of the ion, E is the electric field strength, and K is a constant of proportionality. This constant K is also called the "mobility" of the ion. The mobility of the ion is directly dependent upon both the molecular ion being studied, and the neutral gas through which the ion must drift. A more useful constant which is used in IMS work is the "reduced mobility" of the ion. The reduced mobility of the ion, the mobility of an ion through a gas at standard temperature and pressure, is related to the measured mobility of the ion through the equation

$$K_o = K\ (273.15/T)\ (P/760) \qquad (2)$$

where T is the absolute temperature of the gas in the drift region, P is the total pressure of the gas and the ions in the drift region, and K_o is the reduced mobility of the ion. Because it is often difficult to measure the temperature and pressure within the drift region of the spectrometer, a common practice which is used in determining the identity of ions is to measure the ratio of the reduced mobility of the ion of interest to that of a known species. This known species is usually the reactant ion for the study. If the neutral gas is air, the reactant ions are H_3O^+ when dealing with positive ions, and O_2^- when dealing with negative ions. The ratio of the reduced mobilities are related to measurable quantities through the equation

$$(K_{o1}/K_{o2}) = (K_1/K_2) = (t_{d2}/t_{d1}) \qquad (4).$$

The only parameters which are needed in the analysis is the ratio of the drift times for the ions.

The equation for calculating the mobility of an ion through a gas has been shown to dependent on the first-order collision integral [4,5], which is proportional to the transport cross section. This implies that the mobility of an ion is dependent on the size of the ions, the shape of the ion, and the distribution of charge on the ion; this results in the possibility of more than one ion having the same mobility.

In an ion mobility spectrometer, Figure 1, the sample is introduced through a sample inlet probe. This inlet probe contains a semi-permeable membrane, which allows only a portion of the sample to enter the ionization chamber. The portion of the sample which does not enter the ionization chamber is vented through the exhaust. The carrier flow gas, which is input directly into the ionization chamber and the sample are then exposed to the ionizing source, a ^{63}Ni source in this work. The ions and the gas molecules are then allowed to mix and react in the ionizing chamber. Typical ion reaction schemes which take place in the ionization chamber are shown in Table A. A driving pulse of known shape and duration is then applied to the bipolar gating grid, allowing the mixture to enter the drift region of the spectrometer. While in the drift region, the ions are subjected to an applied electric field (200 V/cm in our studies), which causes the ions to begin their acceleration and collision process. After the ions have traversed the drift region,

TABLE A

TYPICAL ION REACTION SCHEMES

Typical Positive Ion Reactions

$$H^+(H_2O)_n + X \rightarrow H^+X(H_2O)_m + (n-m)H_2O$$
$$H+X(H_2O)_m + X \rightarrow H^+X_2 + m\ H_2O$$

(X is the species to be detected)

Typical Negative Ion Reactions

$$O_2^- + AB \rightarrow O_2 + AB^-$$
$$O_2^- + AB \rightarrow O_2 + A + B^-$$
$$O_2^- + AB \rightarrow (AB \cdot O_2)^-$$

(AB is the species to be detected)

they strike the collector electrode. The signal is then processed to produce the ion mobility spectrum. For those who wish, a more detailed description of ion mobility spectrometry can be found elsewhere [6].

The past several years have seen the advance of ion mobility spectrometry as an analytical technique, with the utility of IMS as an analytical tool for the rapid detection of airborne vapors in the atmosphere being previously demonstrated [7-10], and computer techniques for pre-processing IMS signals have also been presented [11-12].

EXPERIMENTAL

Equipment

Data were collected on an IMS spectrometer [Airborne Vapor Monitor (AVM) from Graseby Analytical, Watford, Great Britain] and stored on an IBM Personal Computer. The data transfer is accomplished using a Graseby Analytical Advanced Signal Processing (ASP) board and its associated software. Each spectrum consisted of 640 data points, which was collected at a sampling frequency of 30 kHz. The other operational parameters of the AVM are shown in Table B.

Vapor Generation

The vapors being used in the linear discriminant data set are generated with a Q5 vapor generator, shown in Figure 2. The Q5 generator has 16 component parts. These parts are: (1) an equilibrator assembly, (2) an air supply (or nitrogen supply) stopcock, (3) a constant pressure regulator (stabilizer) for the air supply, (4) two sampling bubblers filled with solvent (the bubbler is not shown Figure 2), (5) a flowmeter (manometer) for the air supply, (6) a constant pressure regulator (stabilizer) for the diluent air supply, (7) stopcocks for the stabilizers, (8) a stopcock shut off the flow of air from the equilibrator to the mixing chamber, (9) a flowmeter (manometer) for the diluent air supply, (10) a mixing chamber, (11) a reservoir, (12,13) sampling stopcocks, (14) a reservoir exhaust stopcock, (15) a charcoal trap on the exhaust of the reservoir (not shown in Figure 2), and (16) a charcoal canister on the sampling line after the SAW device (not shown in Figure 2).

The equilibrator assembly is the liquid test reagent container of the dilution apparatus. Dry air, under a constant controlled pressure, flows into the equilibrator. This air stream passes over the surface of the test reagent, and becomes

TABLE B

OPERATIONAL PARAMETERS FOR THE AVM

Number Of Waveforms To Be Summed	-	32
Number Of Samples Per Waveform	-	640
Gating Pulse Repetition Rate	-	40 Hz
Gating Pulse Width	-	180 uS
Delay To Start Of Sampling	-	0 uS
Sampling Frequency	-	30 KHz
Gating Pulse Source Is		** External **

saturated with the reagent vapor. The equilibrator is maintained at a constant temperature of 25 ^{o}C by partial immersion in a constant temperature water bath. Included in the equilibrator is a porous alumina cylinder (from Thomas Scientific, Swedesboro, N.J.) to produce a greater surface area for the liquid-vapor equilibration. The dry air-test vapor mixture flows from the equilibrator assembly to the mixing chamber where it is diluted with dry air to the required concentration of milligrams test vapor per liter of dry air.

The flow of air through the equilibrator is controlled by an in-line stopcock, a constant pressure regulator, and a flowmeter. The stopcock is located at the inlet of the equilibrator, and acts as the shutoff valve for the air supply, from the flowmeter to the equilibrator. The constant pressure for the air supply is maintained by bubbling the dry air through a constant level of fluid, e.g. water, in the stabilizer. By raising or lowering the level of the fluid in the stabilizer, the air pressure controlled. The level of the fluid is raised by adding fluid to the stabilizer, and lowered by draining fluid through the stabilizer stopcock located on the bottom of the stabilizer. Changing the pressure of the air supply in this way increases or decreases the flow of the test vapor through the dilution apparatus. Excess air passing through the stabilizer is vented to the laboratory hood. The flowmeter, or manometer, consists of an inner glass tube, which is graduated in millimeters, and outer glass tube through which the air flows, a glass capillary tube of predetermined bore size, a cover to seal the capillary, and a bulb type bottom filled with colored water, which is connected to the constant pressure regulator. The capillary is calibrated such that the flowrate through the capillary is known for any water height. Thus, the flowrate is determined by the height of the water in the inner tube, and the capillary calibration data. The flowmeter measures the flow rate of the dry air-test vapor mixture in milliliters per minute. The flow rate of the diluent air is controlled in the same fashion as the equilibrator air supply with a larger inside diameter capillary tube. The flowmeter for the diluent air is measured in liters per minute. The nominal concentration of the test vapor can be calculated using the equation

$$C = \{(f * p)/([F + f]*P)\} \quad (5)$$

where C is the nominal concentration of the test vapor in parts-per-million by volume, f is flow rate of air through the equilibrator, F is the flow rate of the diluent air, p is the vapor pressure of the test reagent at the temperature of the experiment, and P is atmospheric pressure. Thus, the concentration

of the test vapor may be easily changed by varying either the flow rate of air through the equilibrator, or by changing the flow rate of the diluent air. In practice, it works best to change the flow rate of the diluent air, when possible, because the efficiency of the vapor generation in the equilibrator decreases at higher flow rates.

The dry air-test vapor mixture from the equilibrator and the diluent air are passed into the mixing chamber located at the entrance of the reservoir. The dilute test vapor is thoroughly mixed by a swirling circular motion of the air in the mixing chamber before entering the reservoir. The reservoir is the container for the diluted test vapor, from which samples are taken for concentration analysis and for testing purposes. There is a charcoal canister located on the exhaust of the reservoir. This canister serves as a scrubber to remove test vapors passing from the reservoir to the atmosphere in the laboratory hood.

Pre-Processing of Spectra for Linear Discriminant Analysis

The pre-processing and data processing procedure used in the linear discriminant analysis is shown in Figure 3. The first pre-processing step is to determine if the spectrum has been collected in the positive (+) or negative (-) mode. This knowledge is important since the Graseby ASP board does not differentiate between the two types of spectra, i.e. the ASP board converts all spectra to positive values. The determination of the operating mode under which the spectrum was collected is made by reading the data file header which includes a single character which is used to designate mode. A preliminary discrimination is made based on the mode; a spectrum collected in the negative mode has no chemical semblance to a spectrum collected in the positive mode. Once the mode has been determined, it is necessary to determine the time at which the reactant ion peak (RIP) appears. The reactant ion for the AVM, O_2^- in the negative mode and H_3O^+ in the positive mode, is the species which transfers the charge to the chemical species being analyzed. The location of the RIP must be determined for each spectrum, if possible, because the location is affected by changes in temperature, pressure, and relative humidity. If no RIP is found, then one must assume the RIP is located at the same time as the RIP for the previous spectrum. After determining the time at which the RIP appears, the spectrum is normalized to create a dimensionless X-axis. To do this, each value on the X-axis was divided by the value position of the reactant ion peak. For negative ion spectra collected at, or near, sea level, the peak position with the maximum intensity between 6.0 and 7.0 milliseconds drift time was used for the identification of the reference ion peak. For positive ion data, a value between 6.5 and 7.5 millisecond drift time was used as a window in which to find the reference ion peak. This reference window is easily adjusted for spectra collected at other altitudes or pressures by multiplying the window values by the ratio of the operating pressure to atmospheric pressure at sea level. This new spectrum also appears as a pseudo-"Reduced Mobility" spectrum which has a dimensionless X-axis corresponding to a Ratio of Drift Times, T_R. Only the data in the range 0.5 to 3.0 along the T_R axis are used. A cubic spline is then applied to the spectra such that every spectrum has the same data spacing with respect to the Ratio of Drift Times axis. The IMS data files used in this study have data points every 0.005 T_R.

LINEAR DISCRIMINANT ANALYSIS

Traditionally, much of the effort associated with the analysis of the IMS spectra has been left to the chemist. In an effort to aid in the preliminary identification, a

personal computer (PC) based spectrum identification package has been developed. This package, written in Microsoft Fortran, uses a linear discriminant function for its identification, and consists of three separate programs. These programs are: IMSDISC, a program which reads selected data files from the PC and builds a discrimination data set; TRAIN, a program which analyzes the discrimination set and calculates the linear discriminant function that best isolates the data of interest from the interferant data; and IMSIDENT, a program which reads the data to be analyzed and identified and calculates its linear discriminant value.

Linear discriminant analysis, one of the most basic forms of pattern recognition used by scientists, is used as a supervised learning technique. In supervised learning techniques, the computer learns to classify the samples being analyzed based on knowledge about the samples; in this study, the samples either belong to the class of chemicals you wish to identify, or they do not. The goal of the learning is to develop a classification rule, the linear discriminant function, which allows the validity of the classification to be tested and ultimately to properly classify unknowns.

The linear discriminant function has the general form

$$g(x) = w_o + \sum_{i=1}^{n} w_i x_i \qquad (6)$$

where w_o is the threshold vector, w_i is the weight vector, x_i is the response vector, and $g(x)$ is the response function. The discriminant function, $g(x)$ is determined by choosing those variables x_i with characteristics which differ between the groups being classified. These variables are then linearly combined and weighted such that the groups are as statistically different as possible. This linear combination of variables is calculated using the perceptron convergence criteria.

The perceptron [13-15] is a pattern recognition procedure which consists updating the weight vector by considering only those patterns, or spectra in this work, which have been misclassified in the training set. Each misclassified pattern is considered in turn, with a fraction of each misclassified spectrum being added to the weight vector. This procedure is continued until all of the spectra are classified correctly, or until it is determined that the procedure fails to converge to a satisfactory solution.

In this software package, the three programs are run separately, but are still inter-related. The first program, IMSDISC, uses a file called NAMES. NAMES is simply the file that contains the names of the individual data files to read, and a value that tells the program whether the file is to be treated as the sample or as an interferant. The data from the individual data files is then treated such that all the files are compatible with respect to time spacing between data points, delay to start of data sampling, and number of data points. To accomplish this, IMSDISC uses a spline function to interpolate and fit the data. After the data has been treated to fill the compatibility requirement, the discriminant threshold is set to zero by multiplying all interferant spectra by negative 1, (-1). The sample spectra are left unaltered. The data is then stored in a discriminant data file.

The second program, TRAIN, develops a linear discriminant based on the perceptron convergence criteria. TRAIN prompts the operator for the name of the input discriminant file that was created with the program IMSDISC. It reads the data from the discriminant data set, accepts input for the values of a scaling factor, between 0.000000001 and 0.1, and the number of iterations to perform using this scaling factor. In practice, it is generally necessary to use a series of decreasing scaling factors and iterations to calculate the linear discriminant function which best differentiates the samples and the interferants. After the linear

discriminant function has been calculated, the linear coefficients are written to a file on the computer disk for use by the last program. These first two programs, IMSDISC and TRAIN, are the time consuming programs and are run only when a new compound is to be added to the database.

The third program in this package, IMSIDENT, uses the linear discriminant values created with the program TRAIN. Thus, it is dependent on the first two programs in the package. IMSIDENT can be used in one of two possible configurations; the first configuration is as a stand-alone program, and the second is that it can be incorporated into a data collection program for real time identification of an unknown environment. In the stand-alone configuration, the program prompts the operator for the name of the data to analyze. The program reads the data, and performs a spline interpolation to make the data compatible with the discriminant data sets. Next, the program reads a file named COEF.FIL that contains the names of the coefficient files. The linear discriminant value is then calculated. If the linear discriminant value is positive, an alarm message is generated which notifies the operator that the spectrum has been identified. No message is generated if the discriminant value is negative. The results of the identification process are then written to a file named ALARM.RPT for later use, and the program then prepares to read the next data file to be analyzed.

In the second configuration, the program functions as a real time monitor. The name of the data file to be analyzed is passed from the data collection program to the IMSIDENT package rather than prompting the operator for the name of the data file to analyze. The spline interpolation is then performed on the data, and the linear discriminant value is calculated. If the discriminant value is positive, the alarm message is generated; no message is generated if the discriminant value is negative. The results of the identification process are written to a file named ALARM.RPT for later use.

DISCUSSION

The program package was developed for use with the Graseby Ionics Advanced Signal Processing (ASP) board, the Graseby Airborne Vapor Monitor (AVM), and a Zenith 286 PC. Using this hardware and the linear discrimination package, it has been possible to identify and semi-quantitate the presence of 15 common chemical vapors in air. These compounds, most of which are of industrial importance, and the levels at which the Occupational Safety and Health Administration (OSHA) have determined them to be hazardous are shown in Table C, with the ion mobility spectra of these compounds shown in Figures 4 through 21. When the software is used in the stand-alone configuration (i.e., separate from the data collection routines) and using the Zenith 286 PC, the presence of these compounds can be determined and the compound identified in less than ten seconds. This includes the time necessary to perform the spline interpolation and the calculation of the discriminant value for the data; however, this does not include the time required to create the discriminant functions.

The results shown in Table D are from the evaluation of a series of files used to determine the presence of N-Methyl Formamide. The "All Clear" report indicates that the IMSIDENT program does not find any similarities between the N-methyl formamide test spectrum and the spectra of the fifteen compounds stored in the database. The report of an alarm indicates that the program did find similarities in the spectra, and the magnitude of the discriminant is a measure of the amount of similarity.

It is not really surprising that there are a number of false positive alarms indicating the presence of diethyl ether. Older

versions of the AVM used an acetone dopant within its detection system, whereas newer versions of the AVM use water vapor in the atmosphere as the dopant. This dopant in the older AVM's results in the presence of an acetone reactant ion. This reactant ion is the ionic species which is responsible for transferring the ionic charge to the chemical compound being studied. All of the spectra used in the discrimination functions were recorded using water as the reactant ion. Thus, the discriminant functions have not been trained to eliminate the possibility of alarming on a spectrum which has an acetone reactant ion peak, and an alarm is reported. Examination of two representative spectra for which an alarm was reported, shows the similarity of the IMS spectrum for the diethyl ether, the lower trace in Figure 22 (ETHER in Table D) and N-methyl formamide background spectrum, the upper trace in Figure 22 (\AVM\DATA\nmfo0000.ACQ in Table D). The location of the reactant ion peak does not appear at the same time as does the diethyl ether peak, however the band shapes are similar. If the discriminant function is trained to ignore the acetone reactant ion peak, one does not get an alarm. Results of identification procedure with the acetone reactant ion peak being ignored is shown in Table E.

TABLE E

File "ALARM.RPT" for
N-Methyl Formamide Analysis
with Acetone Reactant ion Ignored

ALL CLEAR FOR FILE	\AVM\DATA\nmfo0000.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0001.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0002.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0003.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0004.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0005.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0006.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0007.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0008.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0009.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0010.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0011.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0012.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0013.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0014.ACQ
ALL CLEAR FOR FILE	\AVM\DATA\nmfo0015.ACQ

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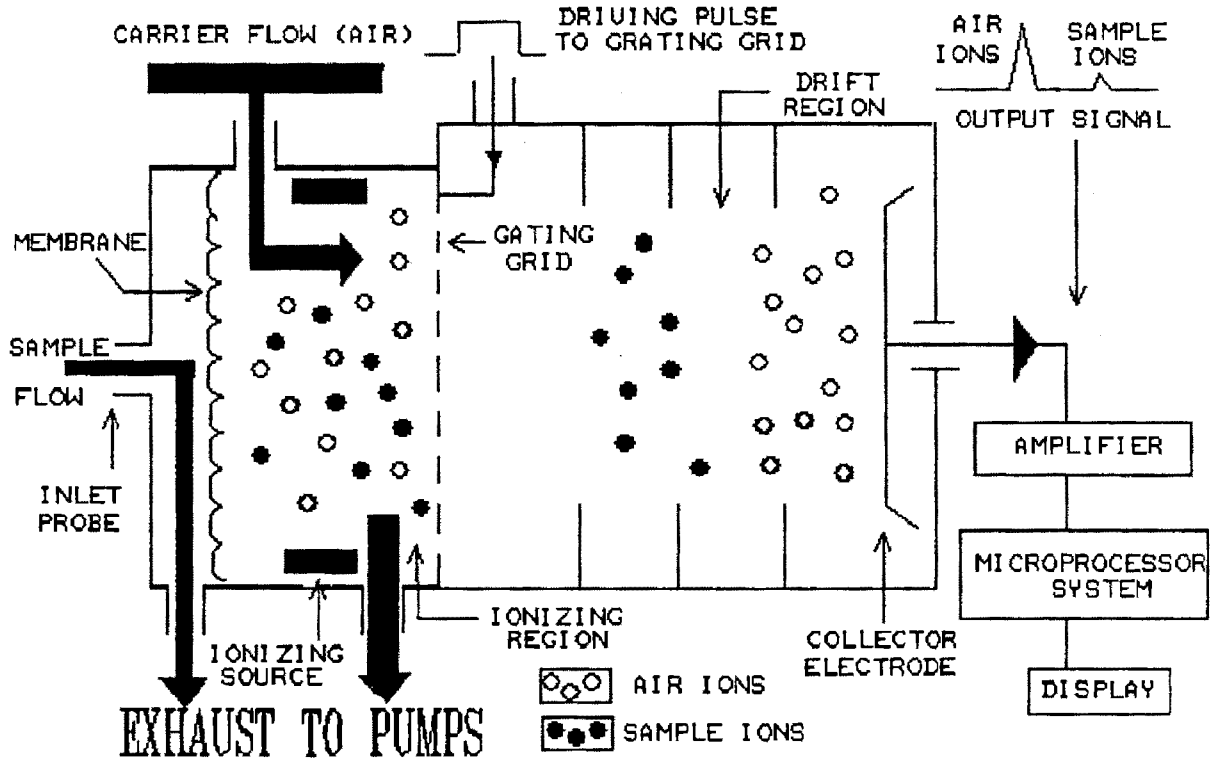

Figure 1. Schematic diagram of an ion mobility spectrometer.

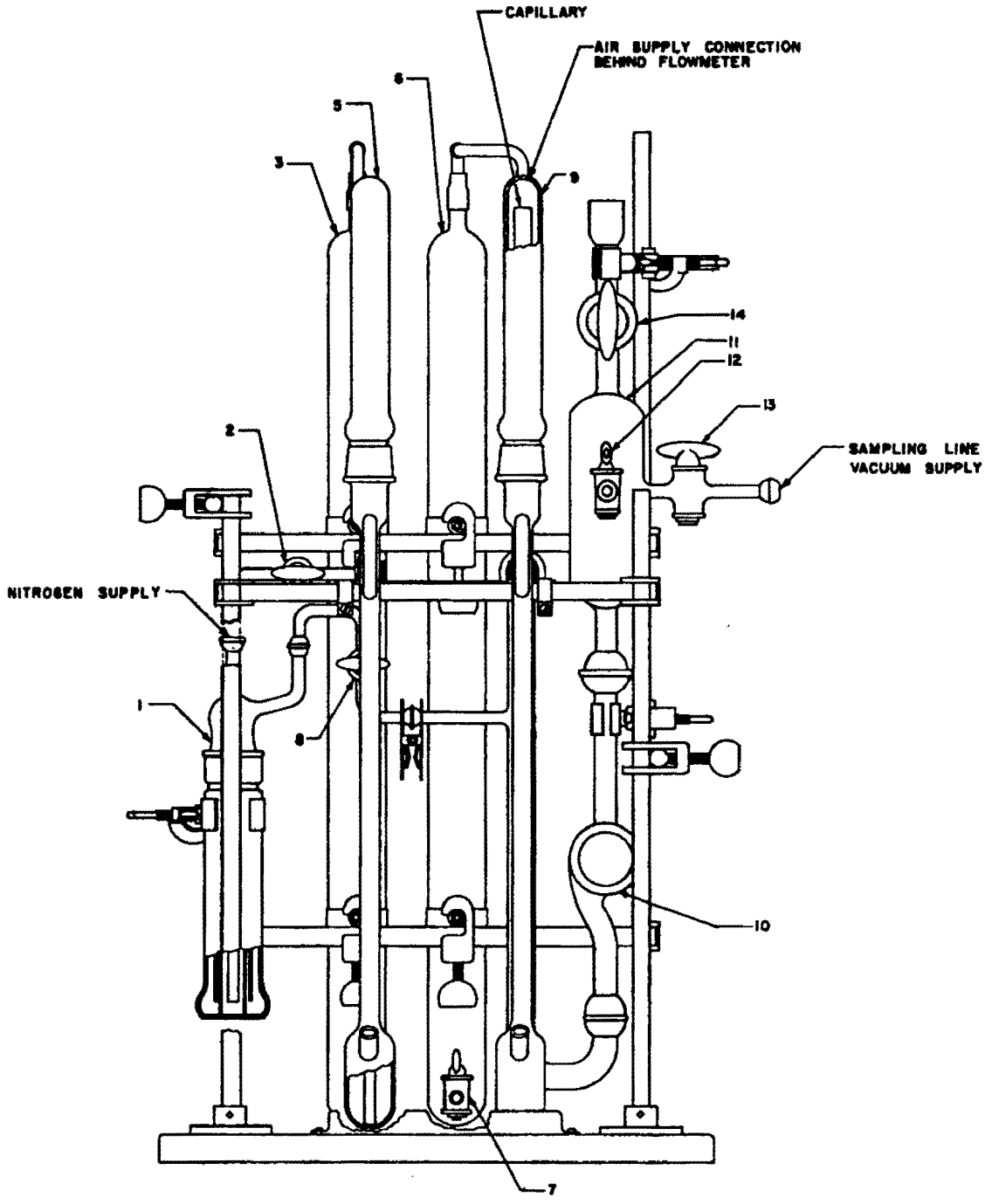

Figure 2. Schematic diagram of the Q5 vapor generator.

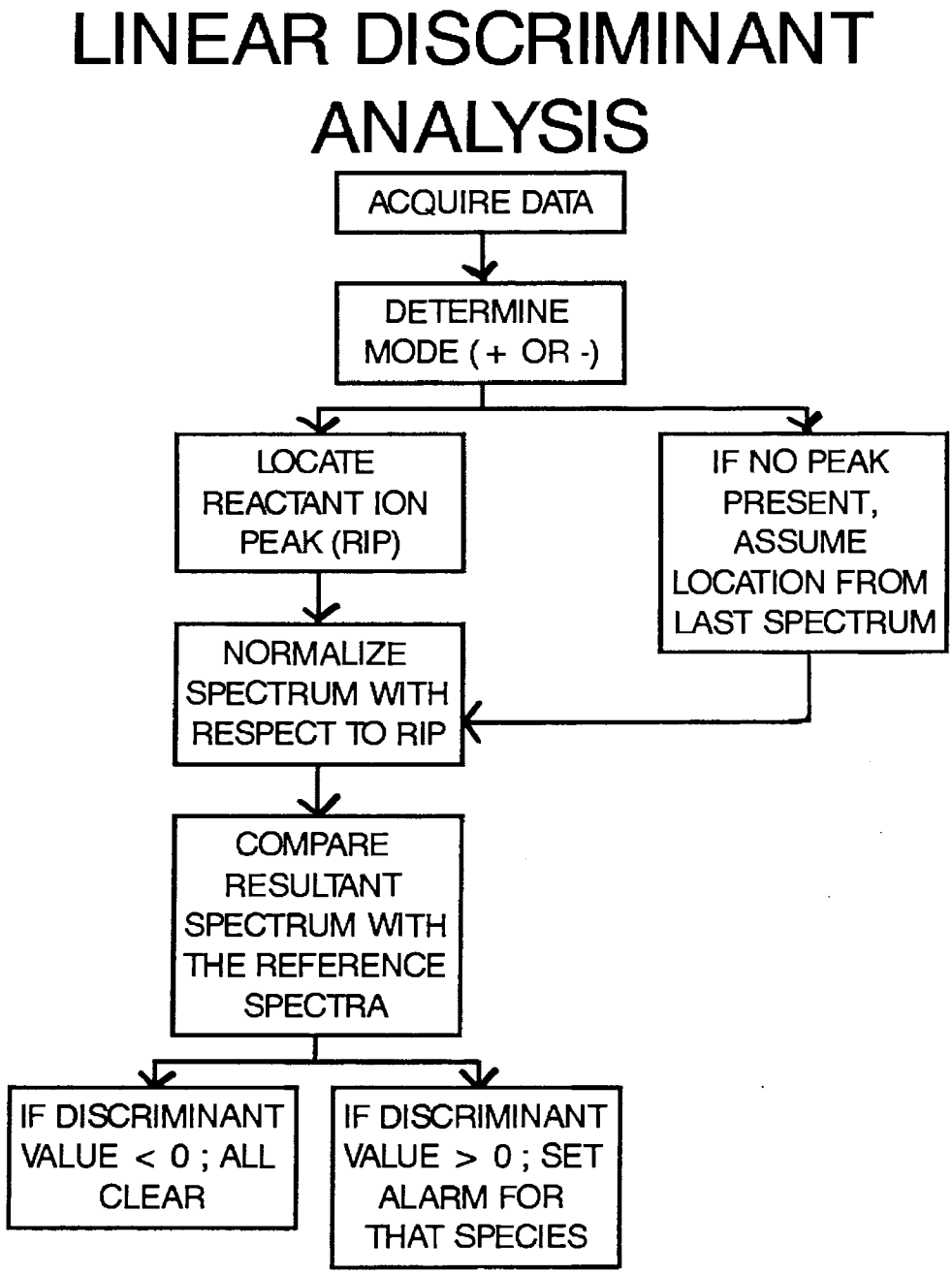

Figure 3. Block diagram showing the steps taken when performing a linear discriminant analysis on an ion mobility spectrum.

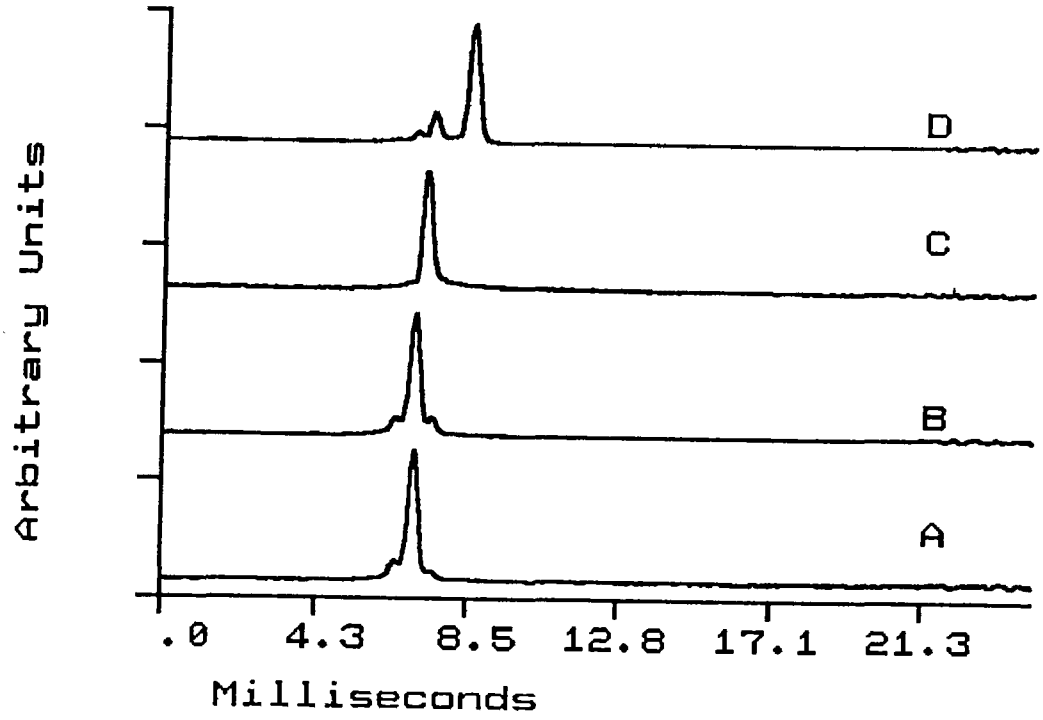

Figure 4. Typical ion mobility spectra of iodine taken in the negative ion mode as a function of concentration. Spectrum A is 2.5 parts-per-billion (ppb) iodine, B is 10 ppb iodine, C is 100 ppb iodine, and D is 1.0 parts-per-million (ppm) iodine.

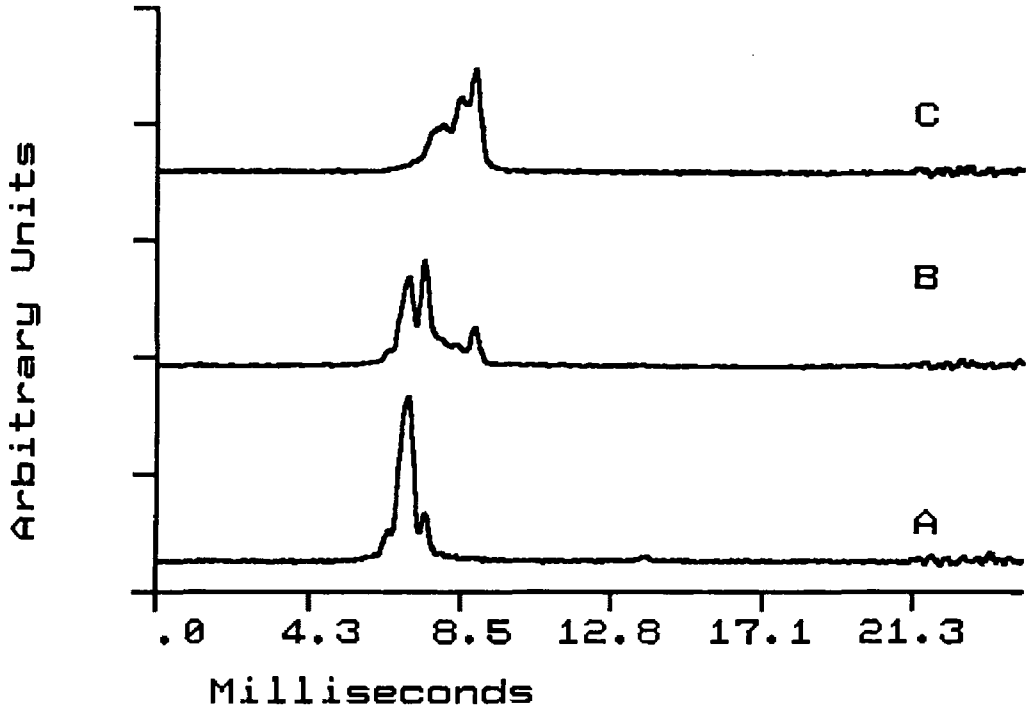

Figure 5. Typical ion mobility spectra of acetic acid taken in the negative ion mode as a function of concentration. Spectrum A is 100 ppb acetic acid, B is 1.00 ppm acetic acid, and C is 10.0 ppm acetic acid.

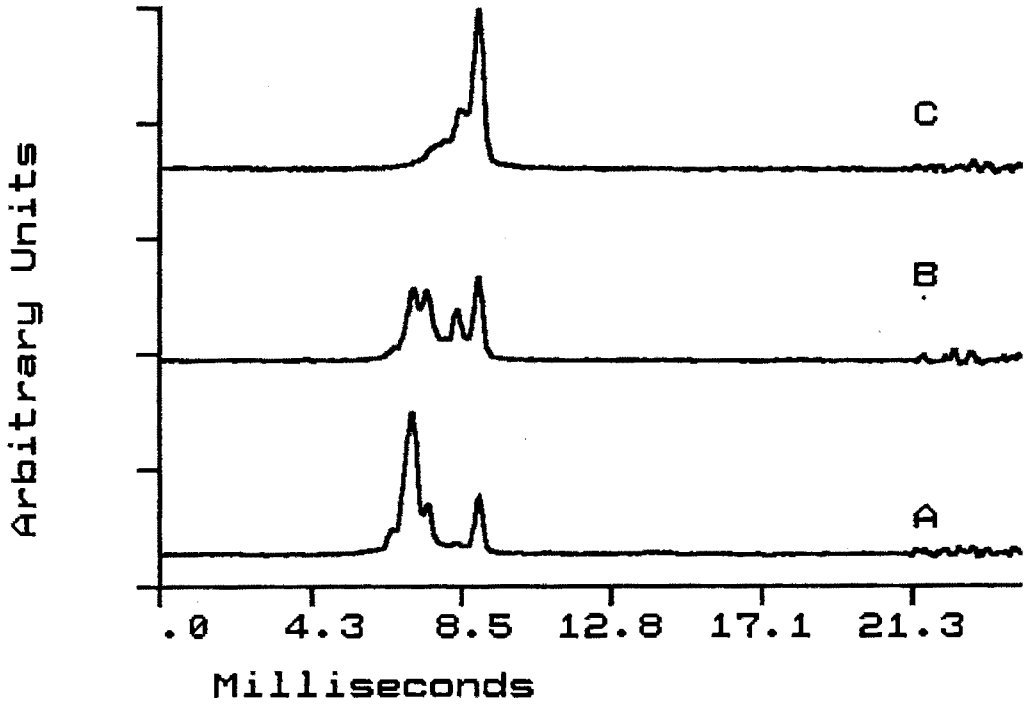

Figure 6. Typical ion mobility spectra of acetic anhydride taken in the negative ion mode as a function of concentration. Spectrum A is 50 ppb acetic anhydride, B is 500 ppb acetic anhydride, and C is 5.0 ppm acetic anhydride.

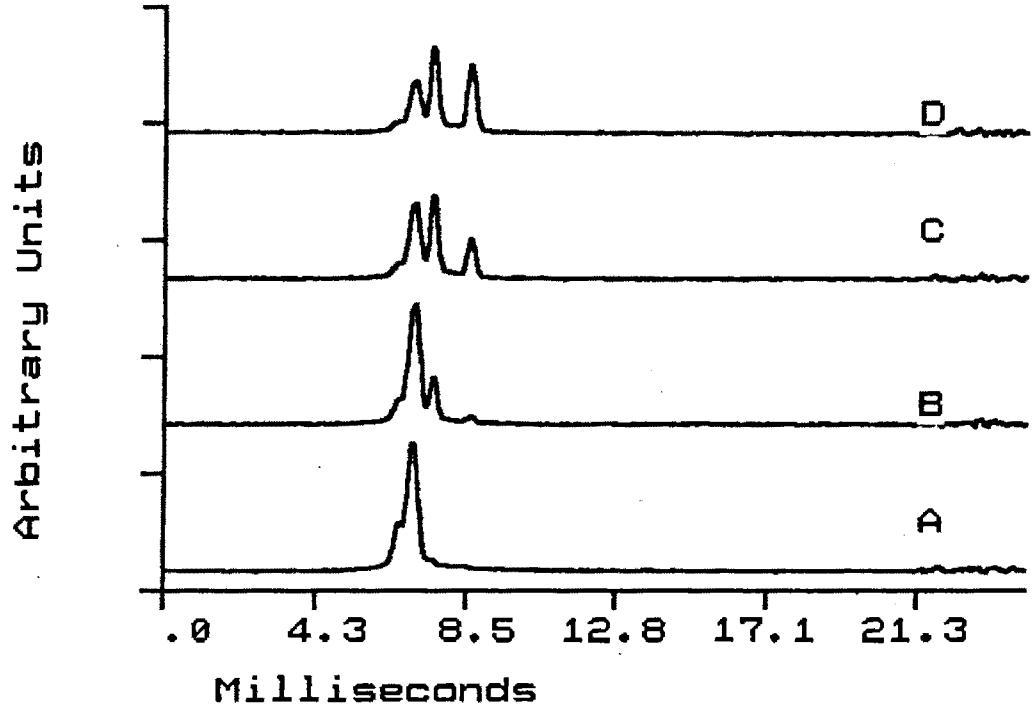

Figure 7. Typical ion mobility spectra of hydriodic acid (HI) taken in the negative ion mode as a function of concentration. HI vapor is generated from a 55% solution of HI in water. Spectra A through D represent increasing concentrations of HI. Actual concentrations of HI have not been determined.

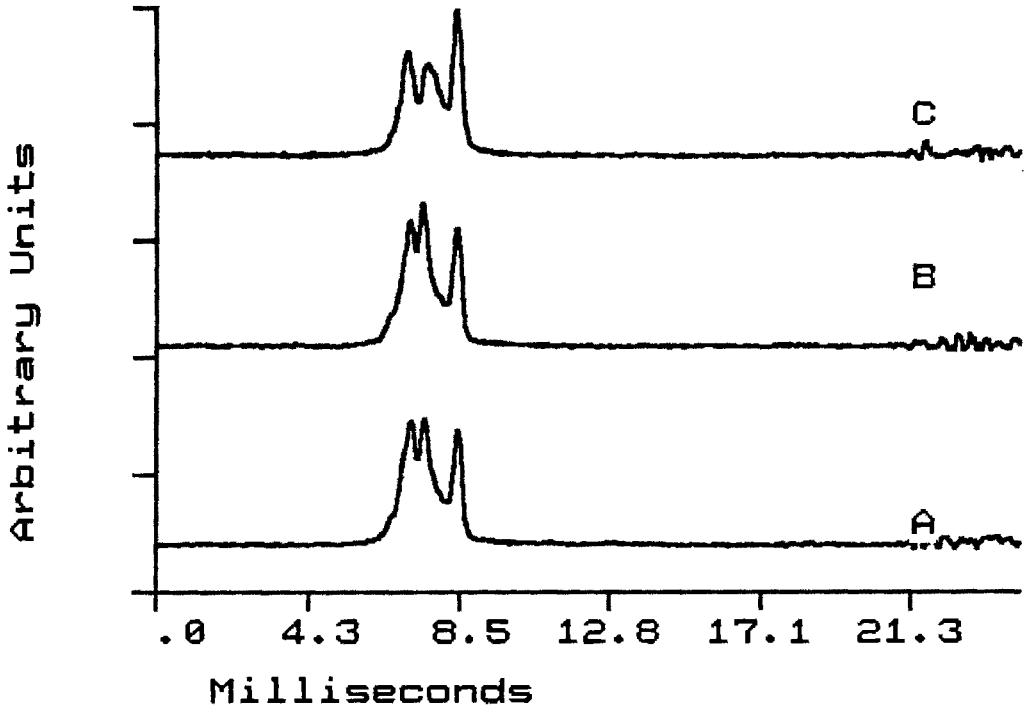

Figure 8. Typical ion mobility spectra of formamide taken in the negative ion mode as a function of concentration. Spectrum A is 300 ppb formamide, B is 3.0 ppm formamide, and C is 30.0 ppm formamide.

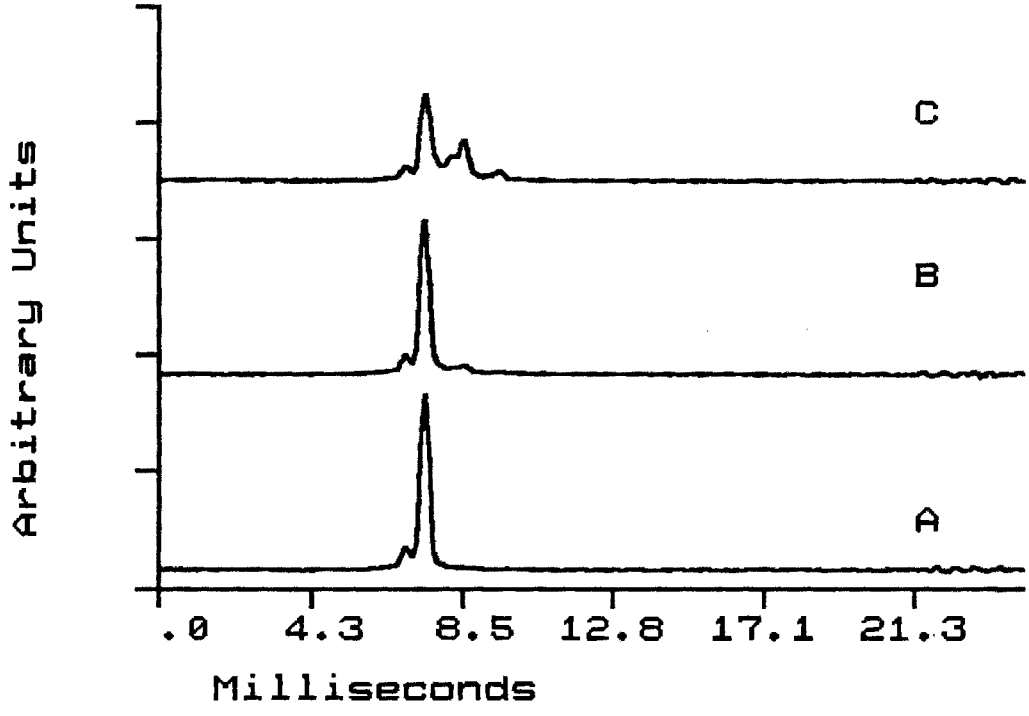

Figure 9. Typical ion mobility spectra of isooctane taken in the positive ion mode as a function of concentration. Spectrum A is 3.5 ppm isooctane, B is 35 ppm isooctane, and C is 350 ppm isooctane.

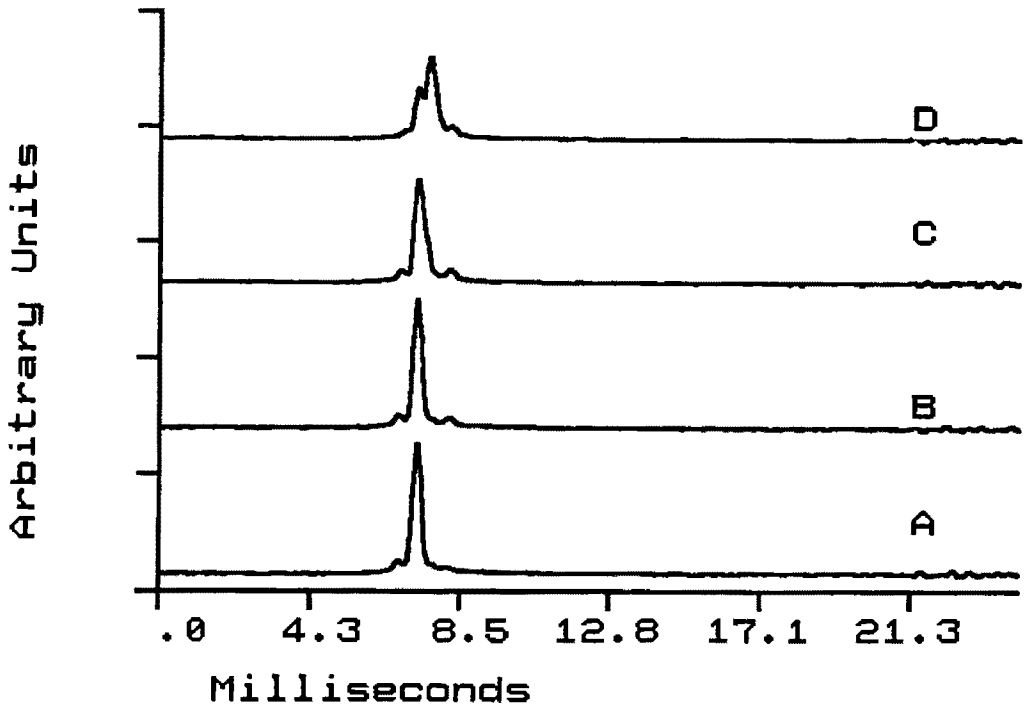

Figure 10. Typical ion mobility spectra of toluene taken in the positive ion mode as a function of concentration. Spectrum A is 15 ppb toluene, B is 250 ppb toluene, C is 1.7 ppm toluene, and D is 10.0 ppm toluene.

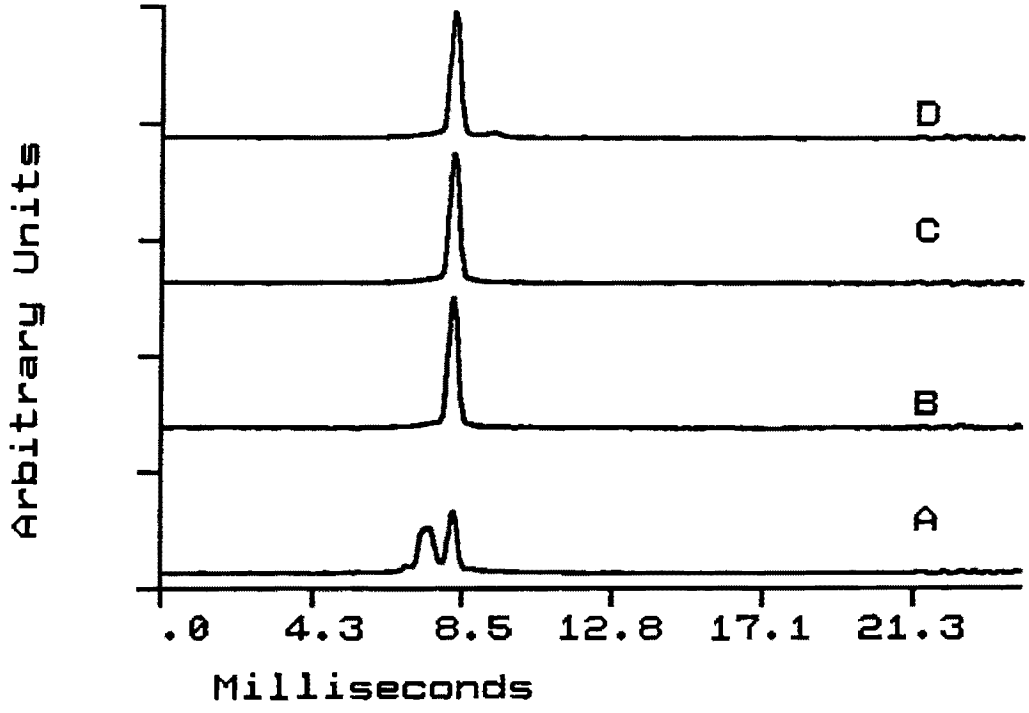

Figure 11. Typical ion mobility spectra of acetone taken in the positive ion mode as a function of concentration. Spectrum A is 1.0 ppm acetone, B is 10.0 ppm acetone, C is 100.0 ppm acetone, and D is 1000 ppm acetone.

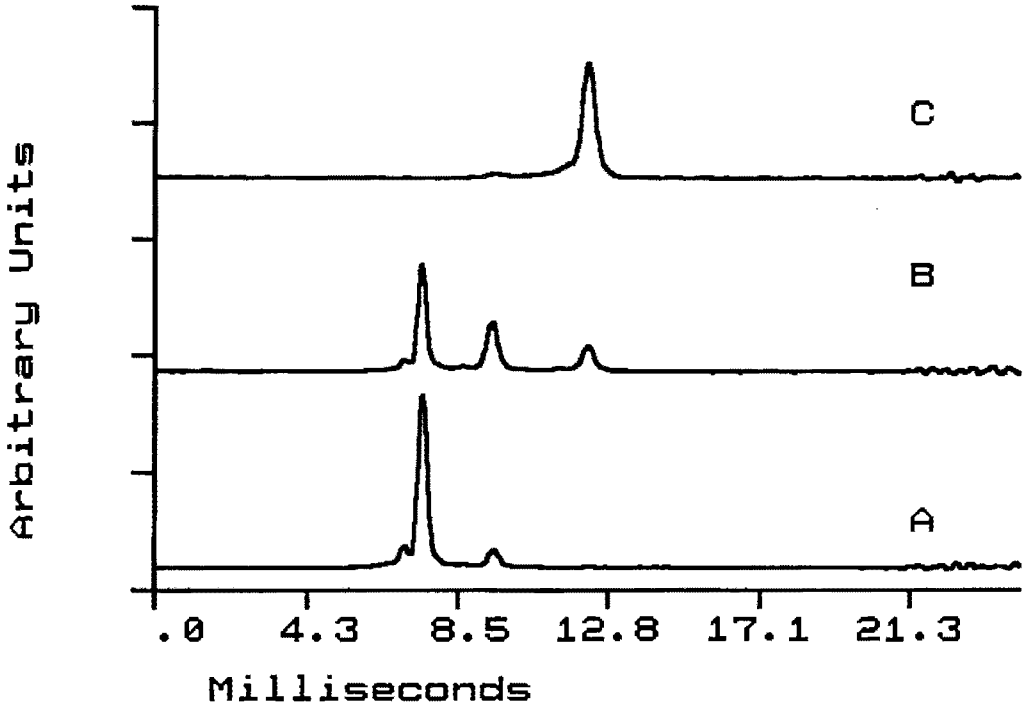

Figure 12. Typical ion mobility spectra of phenyl-2-propanone (P2P) taken in the positive ion mode as a function of concentration. Spectrum A is 10 ppb P2P, B is 100 ppb P2P, and C is 1.0 ppm P2P.

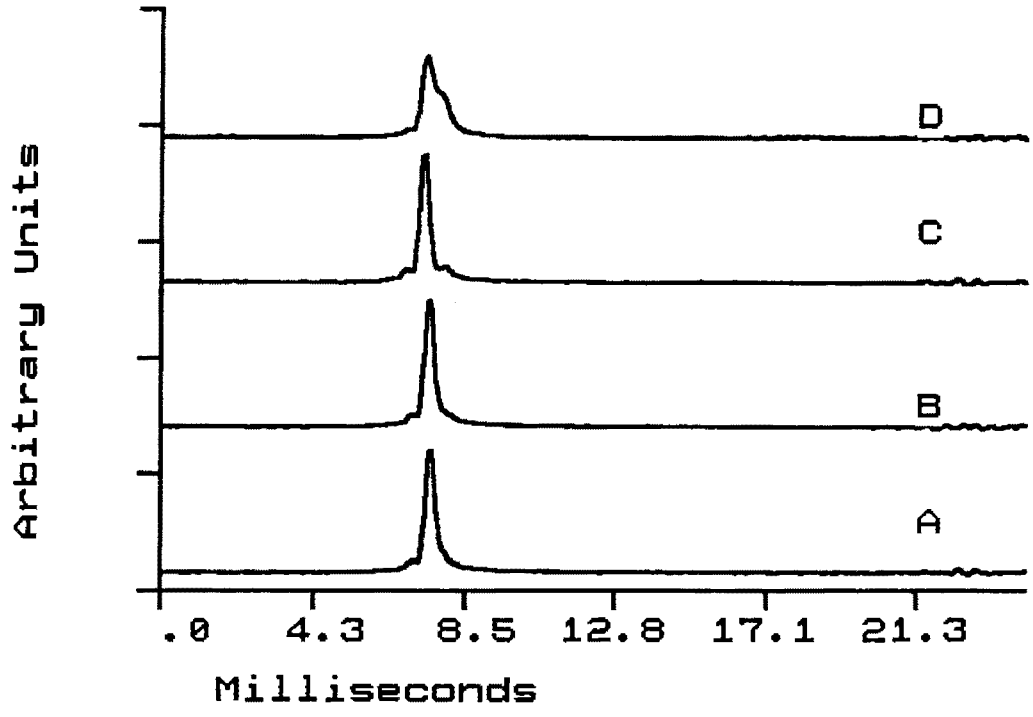

Figure 13. Typical ion mobility spectra of benzene taken in the positive ion mode as a function of concentration. Spectrum A is 250 ppb benzene, B is 1.0 ppm benzene, C is 10.0 ppm benzene, and D is 100 ppm benzene.

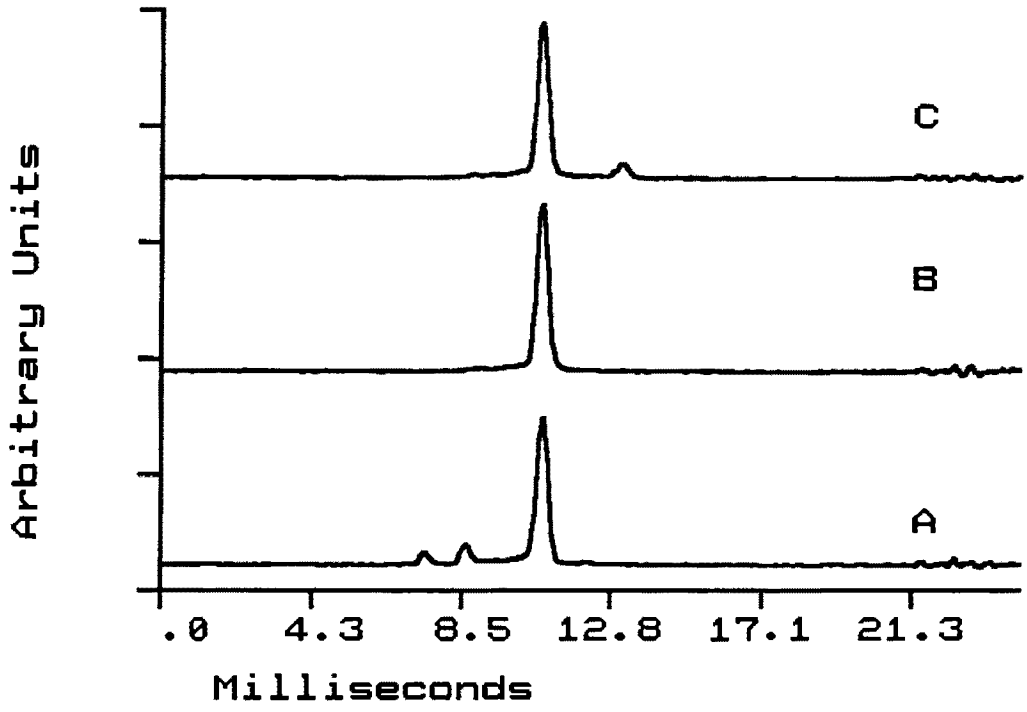

Figure 14. Typical ion mobility spectra of cyclohexanone taken in the positive ion mode as a function of concentration. Spectrum A is 500 ppb cyclohexanone, B is 5.0 ppm cyclohexanone, and C is 50 ppm cyclohexanone.

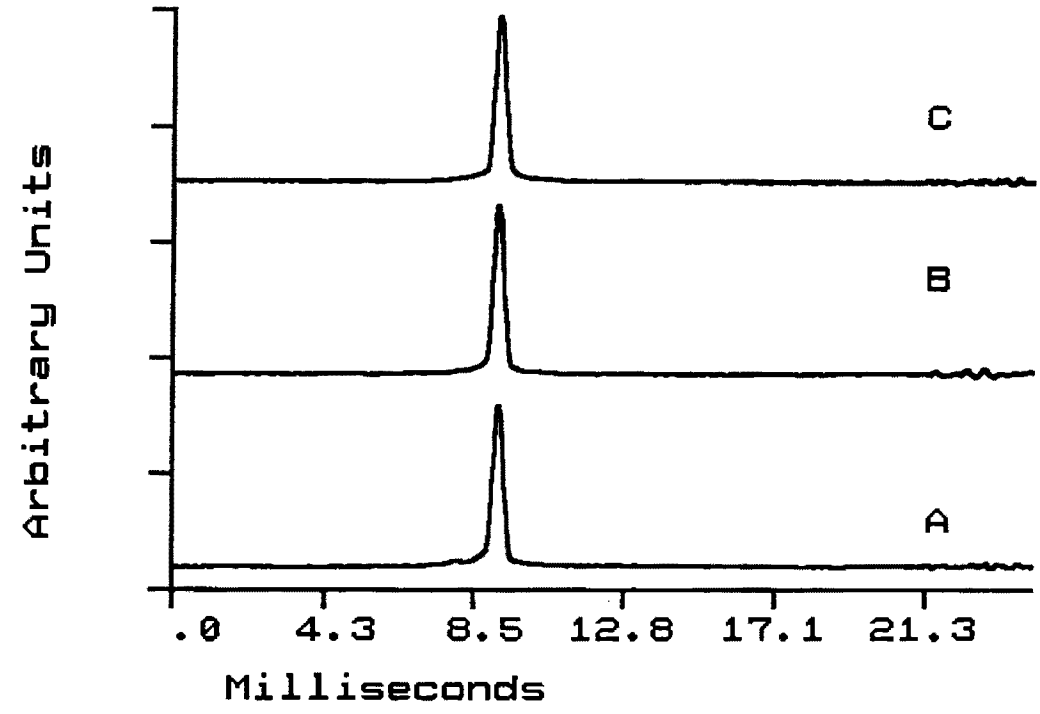

Figure 15. Typical ion mobility spectra of methyl ethyl ketone (MEK) taken in the positive ion mode as a function of concentration. Spectrum A is 3.0 ppm MEK, B is 30 ppm MEK, C is 300 ppm MEK.

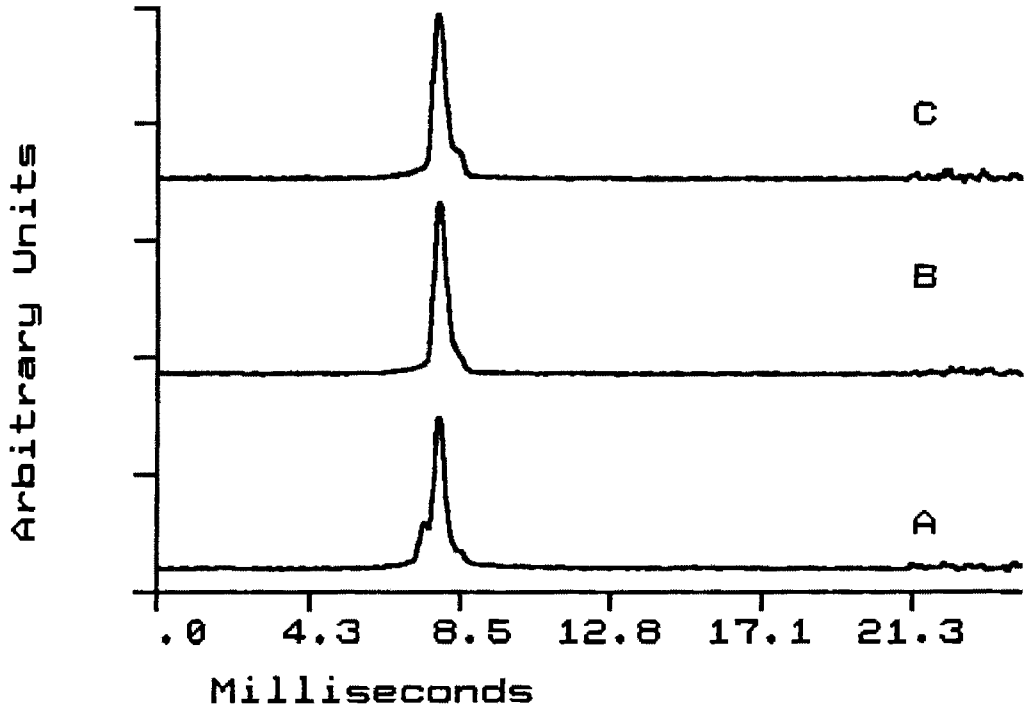

Figure 16. Typical ion mobility spectra of formamide taken in the positive ion mode as a function of concentration. Spectrum A is 300 ppb formamide, B is 3.0 ppm formamide, C is 30.0 ppm formamide.

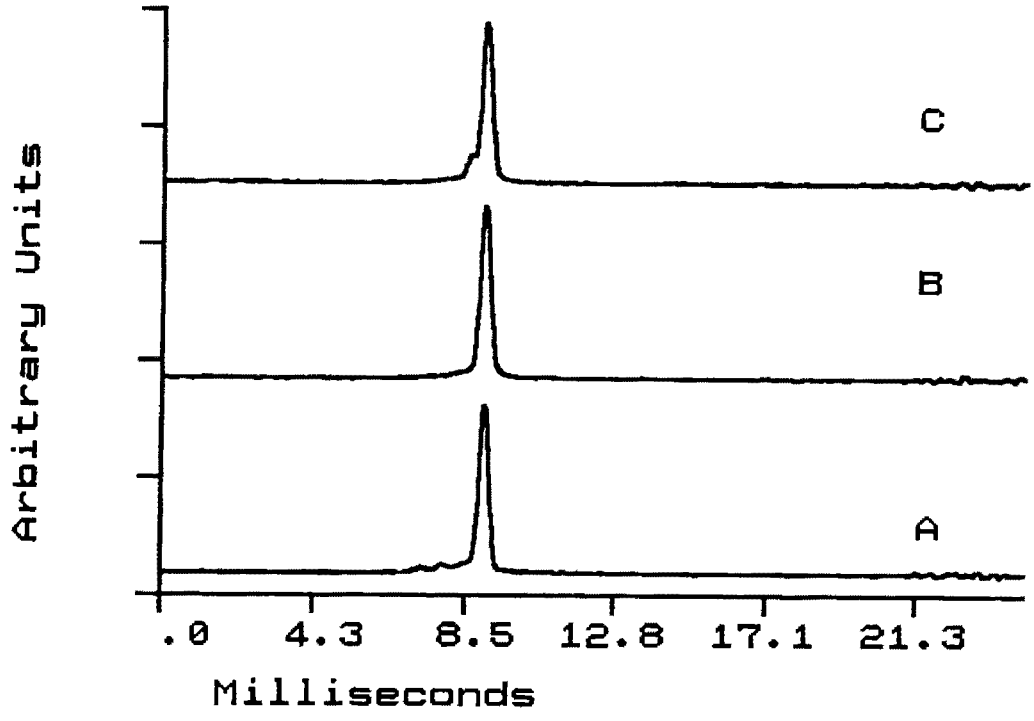

Figure 17. Typical ion mobility spectra of diethyl ether taken in the positive ion mode as a function of concentration. Spectrum A is 4.0 ppm diethyl ether, B is 40 ppm diethyl ether, and C is 400 ppm diethyl ether.

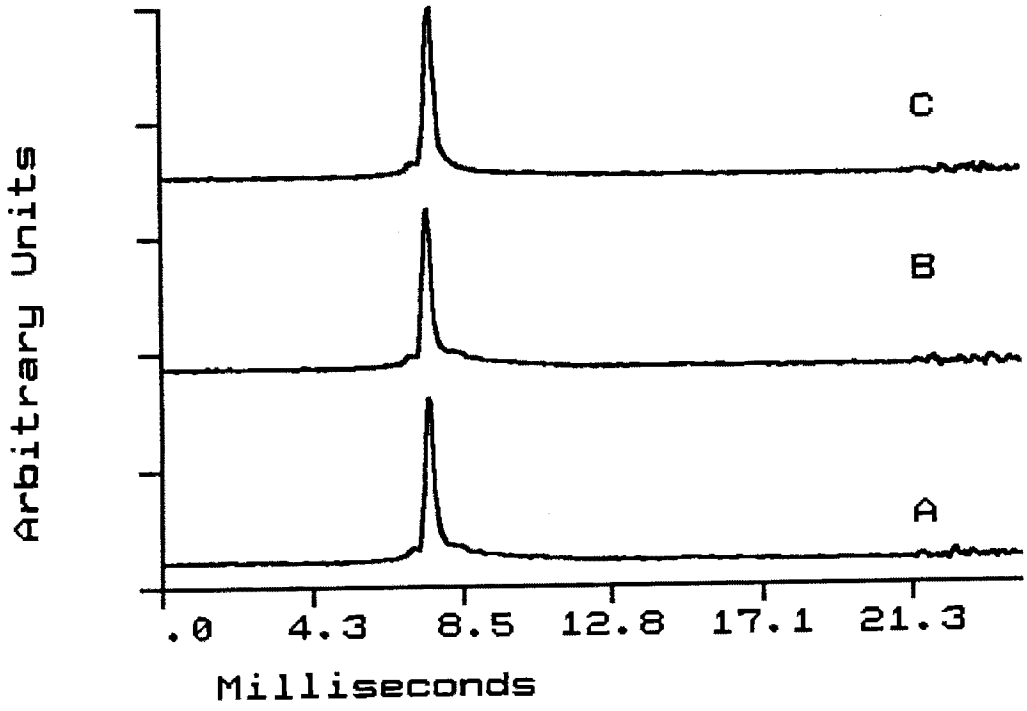

Figure 18. Typical ion mobility spectra of methanol taken in the positive ion mode as a function of concentration. Spectrum A is 8.0 ppm methanol, B is 80 ppm methanol, and C is 800 ppm methanol.

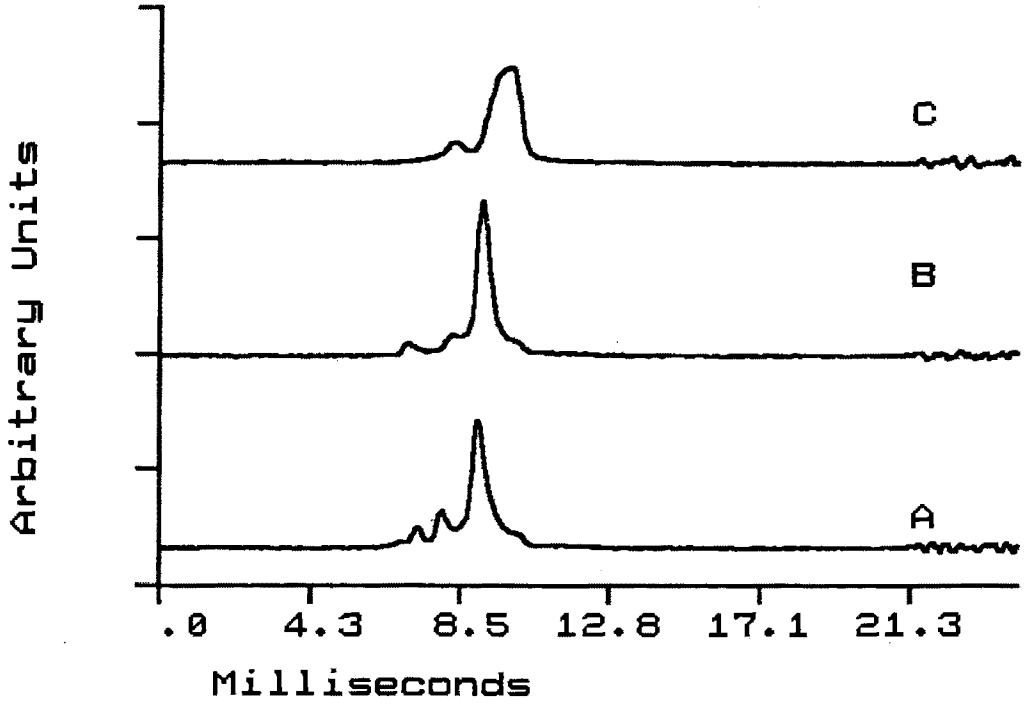

Figure 19. Typical ion mobility spectra of isopropanol taken in the positive ion mode as a function of concentration. Spectrum A is 4.0 ppm isopropanol, B is 40 ppm isopropanol, C is 400 ppm isopropanol.

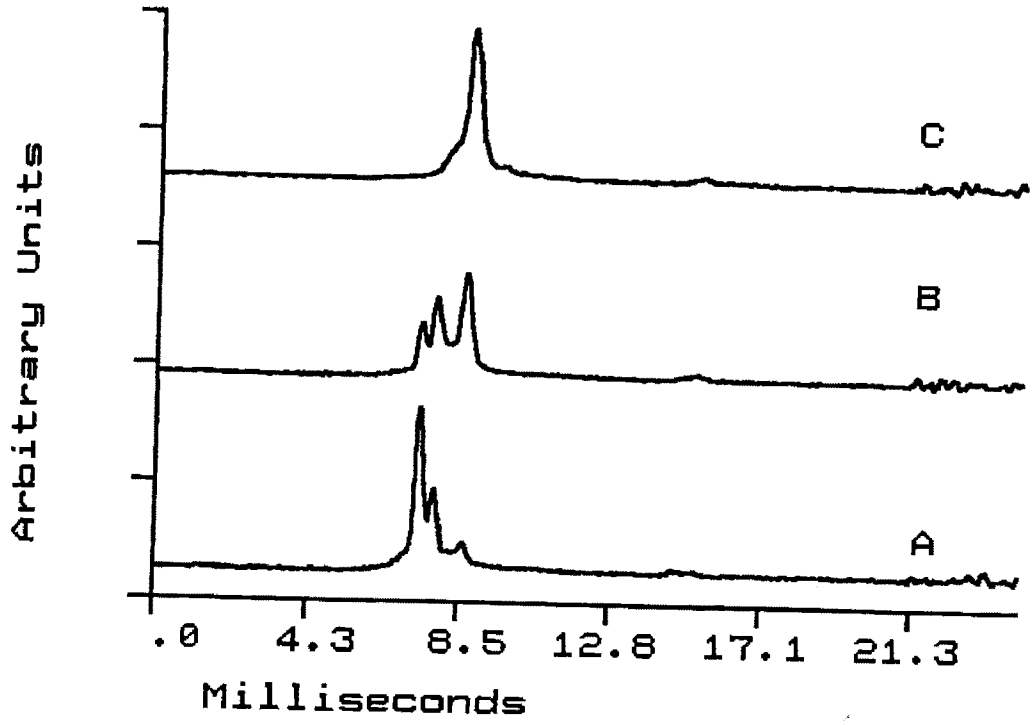

Figure 20. Typical ion mobility spectra of acetic acid taken in the positive ion mode as a function of concentration. Spectrum A is 100 ppb acetic acid, B is 1.0 ppm acetic acid, and C is 10 ppm acetic acid.

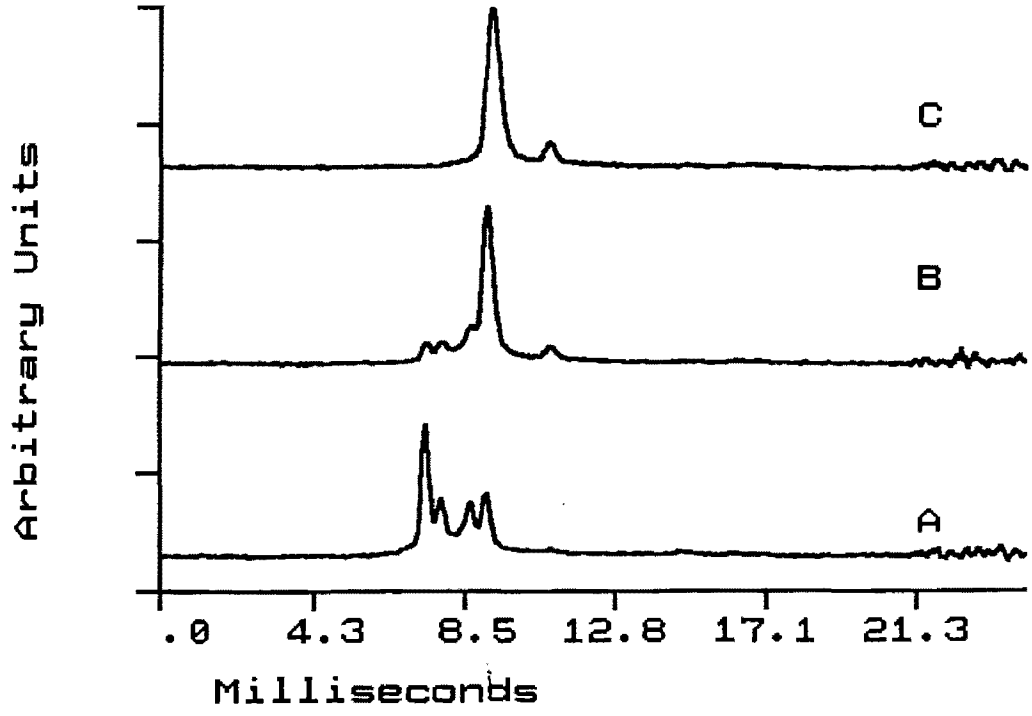

Figure 21. Typical ion mobility spectra of acetic anhydride taken in the positive ion mode as a function of concentration. Spectrum A is 50 ppb acetic anhydride, B is 500 ppb acetic anhydride, and C is 5.0 ppm acetic anhydride.

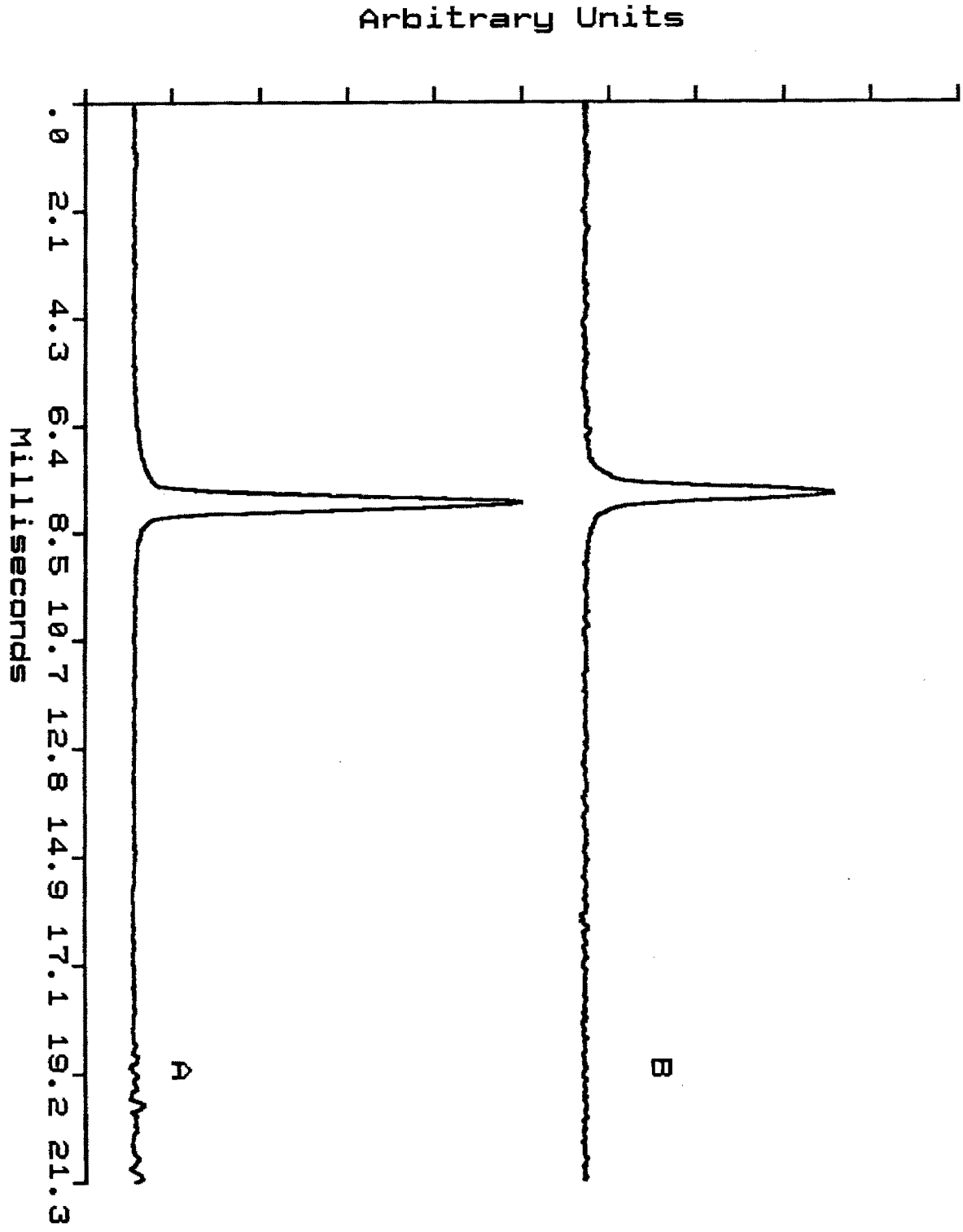

Figure 22. Typical IMS spectra analyzed using linear discriminant analysis. Spectra show the similarities often encountered in IMS spectra. Spectrum A is diethyl ether, and spectrum B is an acetone reactant ion spectrum.

DISCUSSION

DREW SAUTER: Perhaps you could explain certain aspects that have hindered adoption of ion trap mass spectroscopy, basically ion molecule reactions. One of the things I've run into, and others have, is that in certain limited scenarios, you can probably define your ion molecule chemistry.

PETER SNYDER: Yes.

DREW SAUTER: But the truth of the matter, and correct me if I'm wrong, is that you can have unknown reacting ions in the sample. In an unknown situation, it would seem that you could actually get spectra that were sample dependent. Basically, would you see IMS being more useful as a sort of screening tool on relatively limited scenarios, as opposed to a tool that could offer more general analysis capabilities?

PETER SNYDER: Well, I can't disagree with that when you just talk about IMS by itself. Because of the potential complicating responses that can occur if your environment is not controlled, anything can happen.

DREW SAUTER: What I mean though is in the real environmental world, a lot of samples have a lot more than one compound, and not only that do they have a lot more than one compound, recognizing that you can separate things by GC's, they tend to have different concentrations.

PETER SNYDER: Yes.

DREW SAUTER: Hence if they have different concentrations, and there's ion molecule reactions going on, you have them going on with some rate constant. They're producing different populations of ions, and hence a different sample dependent spectra. That strikes me as a significant drawback, despite all the grand things that you've shown.

PETER SNYDER: You have to consider what IMS is based on? IMS is based on ion molecule reactions, and that can be broken down into proton affinity and electron affinity by and large. So then you have to look at what kind of compounds are responding.

DREW SAUTER: But there's also a concentration term that you showed in your graph.

PETER SNYDER: Yes, absolutely. Concentration is very important. I guess the difficulty in response comes then when you get to phosphonate compounds or phosphoryl compounds that are very sensitive to proton affinity. They get that proton very nicely, and by and large to the exclusion of many other compounds, even in their presence, or at relatively high concentrations. Ammonia, probably would take exception too. That might be a complicating factor.

But in most cases, phosphoryl compounds really come through, and that's one of the strengths of the chemical agent monitor, in terms of looking for phosphoryl-based nerve agents.

As you go down to amines, esters, ketones and alcohols, the relative proton affinities are not as wide.

STEVE HARDEN: I'd like to just comment on that before we get on to the next question, and say that yes, you have indeed hit upon one of the problems with ion mobility spectrometry for analyzing real-world mixtures.

The reason the Army has developed it for their purposes is that the compounds they're interested in either have such extreme proton affinities, or extreme electronegativities, and that the sensitivity is very high for those compounds. So it works for our purposes, and it may not work for some environmental purposes that you mentioned, because of this mixture problem.

It also points out one of the needs and requirements in this unknown analysis, or analysis of unknowns, for preparation of sample you mentioned the GC/MS system. We'll hear some more about that in our next paper.

But one can also point out that in some of the data (in this paper) for some compounds that do have a high electronegativity, can be picked out using these techniques that we were talking about, and we can then point out the fact that yes, indeed, that material was present.

That little bump on the side of that peak was, I think, the mustard, which is an Army compound of interest. The bump was on the side of a peak of phenol, phenol being in much greater concentration.

In previous sensitivities and single processing techniques, we can bring it even more if we used preparation of samples. However, you do separate samples at the expense of complexity of instrumentation, and that's one reason why the Army hasn't pursued that to this particular point. So we have.

HERB HILL: For a long time now we have been using ion mobility spectrometers as a chromatographic detector, basically because we feel that there really are problems with interferences, except for very specific cases.

I'm really excited to see us beginning to talk about the use of, what I call chromatographic filters on the front end of IMS, for field monitoring. We've done studies, for example, treating IMS as a chromatographic detector, and you can see that the interferences under conditions like that are no worse than you would have with a flame ionization detector, an electron capture detector. The quantitative value of IMS is acceptable in any range. It's as good as any of the standard chromatographic detectors that we have. We've published papers in which we've put interfering species in, compared them to an FID, and ECD, an IMS, and you see that the quantitative value of the data is fine, it's good in IMS. When you add the chromatograph controls on the front end, you can do dioxins. We do ligands in blood analysis, we do a variety of very small, minute trace compounds in very, very complex mixtures, as well or better, than you can be a lot of techniques.

And it should apply very well to field analysis for portable, if you put a portable GC on the front end of that.

PETER SNYDER: Yes, you're absolutely right. And the literature that you have published over the past decade and a half, attests to that. There's many different sample matrices that Professor Hill has looked at with very good resolution, depending upon the column characteristics. There has been a lot of good information coming out of that, using an IMS as a detector.

So basically the newer innovative topic we're looking at here, is using the hand-held version of the IMS, to see how far we can go with that.

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