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The Analysis of Methamphetamine Hydrochloride by Thermal Desorption Ion Mobility Spectrometry and SIMPLISMA*

REFERENCE: Reese ES, Harrington P deB. The analysis of methamphetamine hydrochloride by thermal desorption ion mobility spectrometry and SIMPLISMA. J Forensic Sci 1999;44(1):68–76.

ABSTRACT: Ion mobility spectrometry (IMS) has been successfully developed to yield an advanced portable instrument. Such instruments may detect trace quantities of regulated substances at the crime scene. The atmospheric ion chemistry that occurs within the instrument may hinder the determination of analytes in real-world samples. The use of temperature programming adds an extra dimension to the data that improves the selectivity of the IMS data when chemometric processing is applied. The SIMPLISMA (SIMPLe-to-use-Interactive Self-Modeling Mixture Analysis) method is demonstrated for modeling variances in IMS data that are introduced from the temperature program. Methamphetamine hydrochloride IMS peaks are obscured by chemical interferences that arise from cigarette smoke residue. Cigarette smoke residue is pervasive at crime scenes. The ability of SIMPLISMA to resolve the analyte peaks that correspond to methamphetamine hydrochloride from interfering cigarette smoke has been demonstrated. A reduced mobility of 1.62 $cm^2V^{-1}s^{-1}$ was observed for a methamphetamine hydrochloride monomer. With the IMS drift tube at room temperature, a second peak was observed at 1.24 $cm^2V^{-1}s^{-1}$, which is consistent with a dimer ion. This peak has not been previously reported.

KEYWORDS: forensic science, ion mobility spectrometry, chemometrics, methamphetamine, substance abuse detection

Ion mobility spectrometry (IMS) is routinely used to screen samples at crime scenes for illicit substances, such as methamphetamine. Cigarette smoke residue prevails at clandestine drug laboratories and interferes with the detection of methamphetamine by generating false positive alarms on IMS instrumentation (1). The reported cigarette smoke residue false positive alarms have been verified on the Barringer Ionscan® 350 in our laboratory.

Detection of the methamphetamine hydrochloride by IMS is important for collecting forensic evidence. Methamphetamine is a controlled substance that is typically produced via the reduction of ephedrine. A rapid and accurate on-site detection method would benefit law enforcement agencies. Current field detection methods use the Ionscan® ion mobility spectrometer to immediately screen vacuumed or swabbed areas prior to transporting the suspected sample to a DEA laboratory for confirmatory analysis (2). A precise method that detects methamphetamine hydrochloride and minimizes the procedures for sample collection would improve the efficiency of evidence collection.

When law enforcement officials enter clandestine laboratories, methamphetamine residues are present in combination with other contaminants including tobacco smoke residues. The ability to differentiate the drug from background interferences is imperative in prosecuting the suspect. Drugs in their salt form have lower vapor pressures and require heating the sample. Heating the sample can produce high concentrations of volatile contaminants that may interfere with the drug peak detection. A common contaminant found at crime scenes is cigarette smoke residue.

Current methods of detection of methamphetamine hydrochloride are performed by flash heating the sample at a relatively high temperature (e.g., 280°C) (1,2). The high temperatures are necessary to furnish adequate vapor concentrations of drugs that are salts. The vapor phase concentrations of interfering analytes are increased as well. False positives and false negatives are of concern when the investigators rely solely on the high temperature desorption in conjunction with an alarm system that is implemented on a Barringer Ionscan® (1). The use of temperature programming adds an extra dimension to the data. This added dimension aids in the interpretation of complex drug spectra, by allowing identification and resolution of analytes in mixtures. Differences in the growth rate of IMS signals, which are caused by differences in vapor pressures or decomposition temperatures of mixture components, may be exploited to separate target analytes from interfering compounds.

IMS has been developed during the last two decades into a useful sensor for the determination of trace quantities of volatile organic compounds. Much of the present interest in IMS can be attributed to the low cost, high sensitivity, fast response, low detection limits, and portability for *in situ* analysis (3). The IMS instrument that was used in this work was a handheld Graseby Ionics Chemical Agent Monitor™ (CAM™). This instrument was modified by removing the acetone reservoir, replacing the internal molecular sieves, and cleaning the instrumental components in a vacuum oven. This modification decreases the selectivity of this instrument, but improves the sensitivity for a wider range of compounds. The CAM™ samples vapors with a pump. The pump draws air through a trifluoroethylene (Teflon™) inlet at a flow rate of 8 cm^3/s. The analytes in the vapor stream permeate across a nonpolar membrane and enter the ionization region of the IMS. Ionization is accomplished by ^{63}Ni beta emission, which initiates a set of atmospheric pressure chemical ionization (APCI) reactions. An ion gate is opened for 0.18 ms, which allows the ions to enter the drift region. The drift region has a linear potential drop that drives the ions to

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* A portion of this work was presented at the Sixth International Workshop on Ion Mobility Spectrometry, August 1997.

Received 30 Oct. 1997; and in revised form 31 March and 11 May 1998; accepted 26 May 1998.

an electrode at the other end of the drift region where the ion current is detected. The opening of the gate initiates the timing of the ions as they travel the length of the drift region. For this instrument, analyte drift times typically fall in a range of 3 to 16 ms. Ion drift time is a function of the potential drop, the volume-to-charge ratio of the ions, and the density of the drift gas.

The Graseby CAM™ differs from the Barringer Ionscan® in several characteristics. A thermal desorption unit is not an integral component to the CAM™. The CAM™ has a nonpolar membrane that separates the inlet region from the ionization region. The CAM™ ion chemistry is based on water that is present in the air. The drift tube and ionization region are operated at ambient temperature, while the Ionscan® is operated at higher temperatures (i.e., approx. 200°C). This difference is important, because cluster ions are not observed at high temperatures. There is no internal calibrant in the CAM™, so one has to be added externally through the inlet.

The advantages of IMS are challenged by the complexities that arise from the APCI reactions. For drug detection, IMS is often used in the positive ion mode. In this mode, product ions (e.g., $M{\cdot}H^+$) are created from the analyte through a sequence of APCI reactions. Increases in analyte concentration may cause the formation of cluster ions (e.g., $M_2{\cdot}H^+$ and $M_3{\cdot}H^+$), and such changes may introduce nonlinear variations into the ion mobility spectra.

Frequently, a proton bound dimer ion ($M_2{\cdot}H^+$) is observed during IMS experiments at low drift tube temperatures (e.g., room temperature). The relationship between peak areas is not stochiometric for cluster ions. In the instance when a proton bound dimer peak has the same peak area as a protonated monomer peak, the proton bound dimer peak will represent twice the analyte concentration of the protonated monomer peak per Eqs (1) and (2).

$$H^+{\cdot}(H_2O)_{m+1} + M \rightarrow M{\cdot}H^+{\cdot}(H_2O)_m + H_2O \qquad (1)$$

The formation of a monomer product ion is given in Eq (1) from a water reactant ion and a neutral analyte (M). At high analyte concentrations protonated dimer ions may form as per Eq (2).

$$M{\cdot}H^+{\cdot}(H_2O)_{m+1} + M \rightarrow M_2{\cdot}H^+(H_2O)_m + H_2O \qquad (2)$$

Competitive charge transfer makes IMS data analysis intricate. Equation (3) typifies the suppression of an analyte signal (M^+) by the introduction of an interferent (N) with greater proton affinity or greater concentration. Only ions are detected.

$$M{\cdot}H^+{\cdot}(H_2O)_m + N \rightarrow N{\cdot}H^+(H_2O)_m + M \qquad (3)$$

In addition, mixed cluster ions may form between the analyte (M) and interferent (N) as given below.

$$M{\cdot}H^+{\cdot}(H_2O)_m + N \rightarrow M{\cdot}N{\cdot}H^+(H_2O)_{m-1} + H_2O \qquad (4)$$

Mixed dimer ions typically produce new peaks in the spectra that occur at an average drift time of the pure dimer ions. The formation of mixed ions may attenuate the analyte peak (M^+). The mixed ion peaks may be correlated with the species of the greater charge affinity and lower concentration.

In the classical IMS experiment, once the instrumental response stabilizes, the spectra are collected and averaged to yield a single spectrum. This approach loses important temporal information that pertains to the measurement period. Using chemometric methods, such as SIMPLISMA, can exploit the changes in the spectrometer response over time to increase the selectivity and sensitivity of the measurement. For the work described later, the temporal information pertains to the sample temperature.

The time required for each IMS measurement is relatively short, so that many spectra can be acquired in a short time. The CAM can collect spectra at a frequency of 40 Hz. If the sample is altered during the course of the measurement, chemometric methods such as multivariate curve resolution may be used to process the data. These curve resolution methods seek to mathematically separate the pure components of a mixture. These methods can be considered as a form of mathematical chromatography. The curve resolution method that is evaluated in this work is SIMPLISMA (SIMPLe-to-use-Interactive Self-Modeling Mixture Analysis) (4–6). For large data collections, peaks may be hidden or distorted by perspective (i.e., information lost) even in the presentation of the data in waterfall or scrolling 3-D displays. SIMPLISMA may also be considered an alternative display method that uses two 2-D graphs to represent the information in the 3-D display of the measurement data.

Major benefits of SIMPLISMA are computational efficiency and simplicity towards the assumptions regarding the concentration profiles. SIMPLISMA has been successfully applied to depth profiling of polymer laminates by infrared spectrometry (7) and assessment of peak purity in liquid chromatography (8). This method has also been used for mixture analysis (9–11), pure component analysis (12), and the detection and characterization of cobalt species in zeolites by diffuse reflectance spectroscopy (13). SIMPLISMA has been used in IMS, although features in IMS tend to vary nonlinearly, and proved useful for the identification of individual cluster ion peaks including mixed cluster ions (14).

SIMPLISMA performs by finding pure variables (PVs) in the data set and uses the pure variable intensities to estimate the concentration profiles of the analytes. A PV is a point in the spectrum that is selective in that it varies correspondingly with a component in a mixture, and does not vary with changes in concentration of the other mixture components. The purity of a drift time variable is an indicator of the variable's selectivity over the measurement period. IMS data has features that vary nonlinearly with respect to concentration changes due to the formation of cluster ions. These features may have characteristic PVs that can be extracted as separate components. The components of the mixture must vary in concentration during the measurement period for SIMPLISMA to work.

The SIMPLISMA algorithm has been published previously and the computation will be briefly described (4,14). SIMPLISMA computes the purity of each drift time for a set of data. The purity is a measure of the relative variations of the intensity values for the drift time multiplied by a measure of independence of the relative variance. The relative variations are similar to relative standard deviations. Because all the intensities of an IMS peak are correlated with respect to measurement time, the purity also must factor in a measure of independence for each drift time point. Variations in intensity that occur at different rates during the experiment will be modeled as different components of a mixture. Variations in intensity that are correlated with respect to the measurement time are modeled as the same component.

The intensities at the drift times that furnish the largest purity values are used to model the concentration profiles of each component. The data matrix is regressed onto the concentration profiles using multivariate linear regression to acquire mathematically extracted spectra. Each spectrum is normalized by the sum of all the positive intensities. Normalization corrects for scale caused by different concentrations. The SIMPLISMA extracted spectra have

relative intensity units, so that the absolute intensity unit will be represented by the concentration profile. The data matrix is regressed onto the normalized spectra to furnish concentration profiles that have the same units as the instrument readout (i.e., mV).

Determination of the correct number of components or PVs is accomplished by visual examination of concentration profiles and extracted spectra. The SIMPLISMA calculation is rapid and can be accomplished on a personal computer in less than a minute, so an arbitrary number of components is selected. The extracted spectra and concentration profiles are examined in the order they are calculated. Extracting too many components will overfit the model to the data. Overfitting produces components that model noise, small shifts in the peaks, or peak shape variations. Overfitting can be detected by splitting of the reactant ion peak or extracting spectra that contain low signal-to-noise ratios. For example, the standard methamphetamine hydrochloride data yielded four components, because the fifth component modeled a small shift with respect to drift time of the reactant ion peak. Therefore, the calculation was rerun with the number of components set to four.

The SIMPLISMA method can also be applied to spectra collected from several different experiments that have been combined into a single data set. SIMPLISMA assumes that the analyte concentration varies independently of the background matrix. This assumption may or may not be true. If the assumption is incorrect then some of the extracted components may contain features that are from both analyte and background signals.

Methods

(+)-Methamphetamine hydrochloride (Sigma Chemical lot number 31H0454) was investigated in this study. For the calculation of reduced mobility values (K_0), 2,4-lutidine (Acros Organics lot number 58411/2) was used. The ion mobility spectrometer used in this work was a CAM™ Type 482-301N (Graseby Ionics, Ltd. Watford, Herts, U.K.) and was used with a single modification. The reagent chemistry was based on water rather than acetone. The modification removed the reagent gas source from the recirculating gas system of the CAM™. The molecular sieves were replaced and the internal components of the CAM™ were baked at 100°C in a vacuum oven for several hours.

All spectra were acquired in positive ion mode. Each spectrum was acquired as 64 averaged scans that were composed of 1300 data points. The data acquisition frequency was 80 KHz. The gating pulse frequency was 40 Hz with a width of 180 μs. Spectra were collected with a 1.0 ms delay and at a rate of 16 spectra/min.

An aluminum block that was 9.0 cm × 6.0 cm × 2.0 cm was bored so that it would hold a 150 mL beaker (i.e., sample compartment) and provide good heat conduction between the beaker and a hot plate. A 4.5 cm diameter, 6.0 cm in length, and 1.0 cm deep semi-cylinder was bored out of the aluminum block to hold the beaker. At a position 3.0 cm along the length and 1.5 cm below the boring, a 4.0-cm-deep hole was drilled for the insertion of a thermometer.

Three sets of data were collected. A 150 mL graduated glass Pyrex beaker was set on its side on an aluminum block and placed on a hot plate (Thermix Stirring Hot Plate Model 310T Allied Fisher Scientific). Each data set, for both parts of the data collection, contained 25 blank spectra. Between experiments, the beaker was cleaned and the aluminum block was cooled to room temperature. The CAM was placed on a clean dry air line and was not used until it returned to a baseline (i.e., no analyte) response.

The target analyte was methamphetamine hydrochloride. A few crystals (1 mg) of methamphetamine hydrochloride were placed at the 60 mL mark inside the beaker (26 mm from the bottom of the beaker). The beaker was heated to 190°C in approximately 1 h and 15 min. For the second experiment, a small scraping of cigarette tar (1 mg) was placed at the 60 mL mark on the beaker and the beaker was heated as before. The cigarette tar came from burning 12 cigarettes of several commercial brands on a watch glass and collecting the smoke in a beaker. The brown tar was scraped from the sides of the beaker. The third experiment collected spectra from a mixture of the cigarette tar scrapings (1 mg) and a few crystals of methamphetamine hydrochloride (1 mg) that were heated to approximately 190°C. For all three experiments, the tip of the IMS was placed at the mouth of the beaker. The ambient air was laboratory air, and the experiment was conducted inside a fume hood.

The source code was written in single floating point precision (32 bit) C++, and was compiled with the Watcom® C++ 11.0 compiler that generated a 32-bit flat memory mode executable for Microsoft® Win32S™, Win95™, and WinNT™ operating systems. The code was optimized to generate the fastest executable code for a Pentium Pro® computer that ran as a character mode executable.

The code was executed on a single processor Pentium Pro® 200 MHz computer equipped with 64 MB of RAM. The personal computer used the Microsoft® Windows NT™ 4.00.1381 operating system. The SIMPLISMA bias value (α) was set to 10% of the largest intensity value in the data set. Each spectrum was baseline corrected by calculating the average intensity between 1.5 and 3.0 ms, and then subtracting this average from the intensities in the spectrum. Only the drift time range of 4.0 to 10.6 ms was used for SIMPLISMA.

The spectra were all collected until a temperature of 190°C was obtained in the beaker. Because a hotplate was used for heating the samples, the heating rates varied among experiments. The number of spectra that were collected in each experiment due to the different heating rates varied as well. The standard methamphetamine consisted of 1200 spectra acquired from methamphetamine hydrochloride. The standard smoke tar data set consisted of 975 spectra acquired from cigarette tar. Methamphetamine hydrochloride combined with smoke tar was composed of 1015 spectra acquired from the mixture. The variation of the number of spectra and heating rates should not affect the results, because the standard runs are only used to verify the identities of components in the drug/smoke residue experiments.

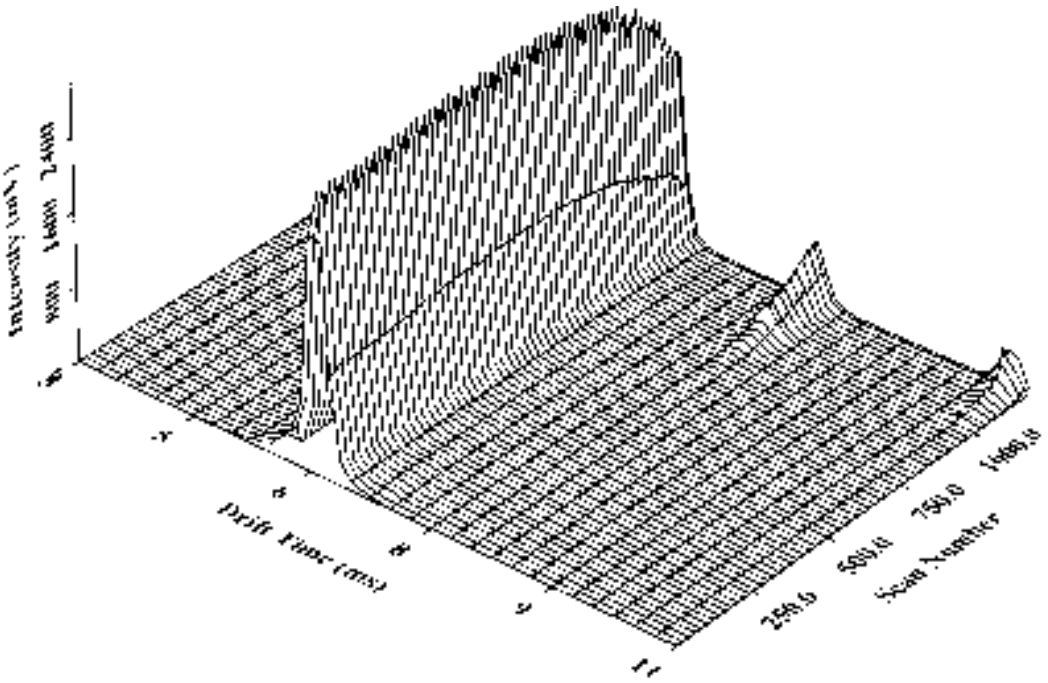
Drift times are often reported as reduced mobilities (K_0) that correct for variations among instrumental factors such as drift tube length and drift potential, as well as environmental factors such as pressure and temperature of the drift region. Reduced mobilities are useful for comparing results among instruments and laboratories, and provide qualitative information that may be used for identification. Reduced mobilities were calculated using 2,4-lutidine as the internal standard. The reference reduced mobility value was 1.41 $cm^2V^{-1}s^{-1}$ which corresponds to the 2,4-lutidine dimer peak (15). The reduced mobility is calculated by the following equation:

$$K_0(\text{unk}) = \frac{K_0(\text{std})t(\text{std})}{t(\text{unk})} \quad (5)$$

for which K_0 is the reduced mobility in units of ($cm^2V^{-1}s^{-1}$) and t is the drift time of the standard (std) and unknown (unk).

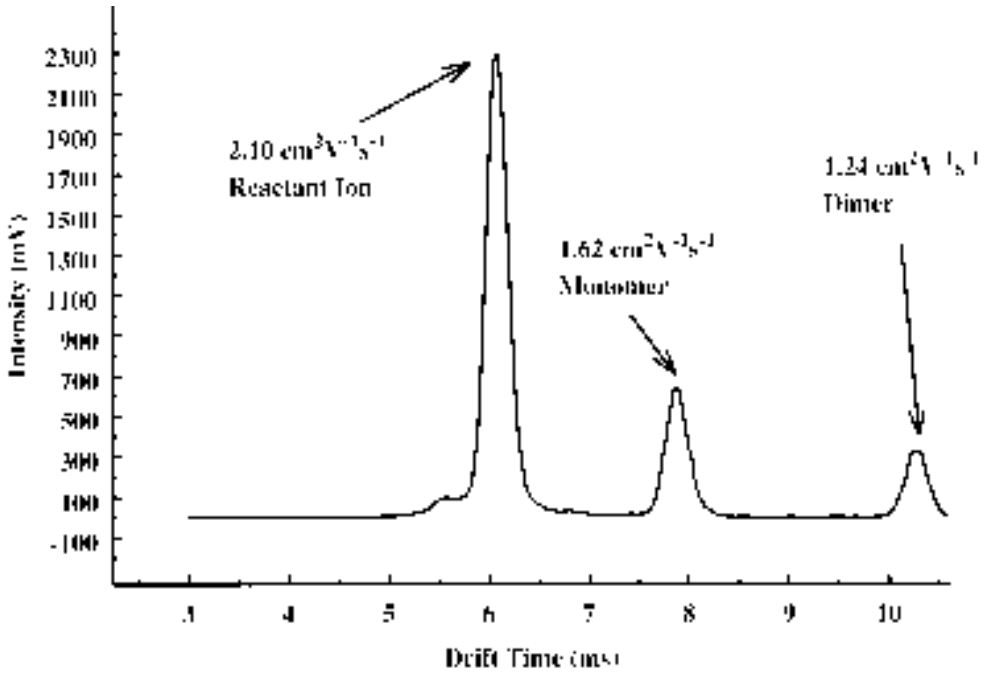
Discussion

For each experiment a set of temperature programmed data is obtained. The data obtained from the methamphetamine hydrochloride are given in Fig. 1*a*. Figure 1*b* gives the representative



A

FIG. 1*a—Surface plot of methamphetamine hydrochloride data set that gives ion current as a function of drift time and scan number.*



B

FIG. 1*b—Positive ion mobility spectrum of methamphetamine hydrochloride with reduced mobility values at scan number 1200, collected at a temperature of 190°C.*

spectrum of methamphetamine hydrochloride with the calculated K_0 values. Table 1 displays the results from the reduced mobility calculations and reports previously published values for methamphetamine. The standard deviations measure the experimental repeatability using the same instrument, but different samples and different days of analysis. Reduced mobility is a very robust figure of merit.

With methamphetamine hydrochloride, the experimental monomer peak has a reduced mobility of 1.62 $cm^2V^{-1}s^{-1}$ while the literature value is 1.6441 $cm^2V^{-1}s^{-1}$. Both of the experimental values are comparable to the literature values although the samples were run on different instruments that operated under different conditions (2). The methamphetamine dimer peak was not observed at the high drift tube temperatures used by the Ionscan®

TABLE 1—*Experimental reduced mobilities.*

Reduced mobilities with experimental Standard Deviation ($cm^2V^{-1}s^{-1}$)	Reactant Ion (water)	Peak 1	Peak 2
Cigarette smoke	2.11	1.85	1.56
literature value for nicotine (1)	. . .	. . .	(1.55)
Methamphetamine hydrochloride	2.10 ± 0.003	1.62 ± 0.001	1.24 ± 0.002
literature value (2)	. . .	(1.6441)	. . .

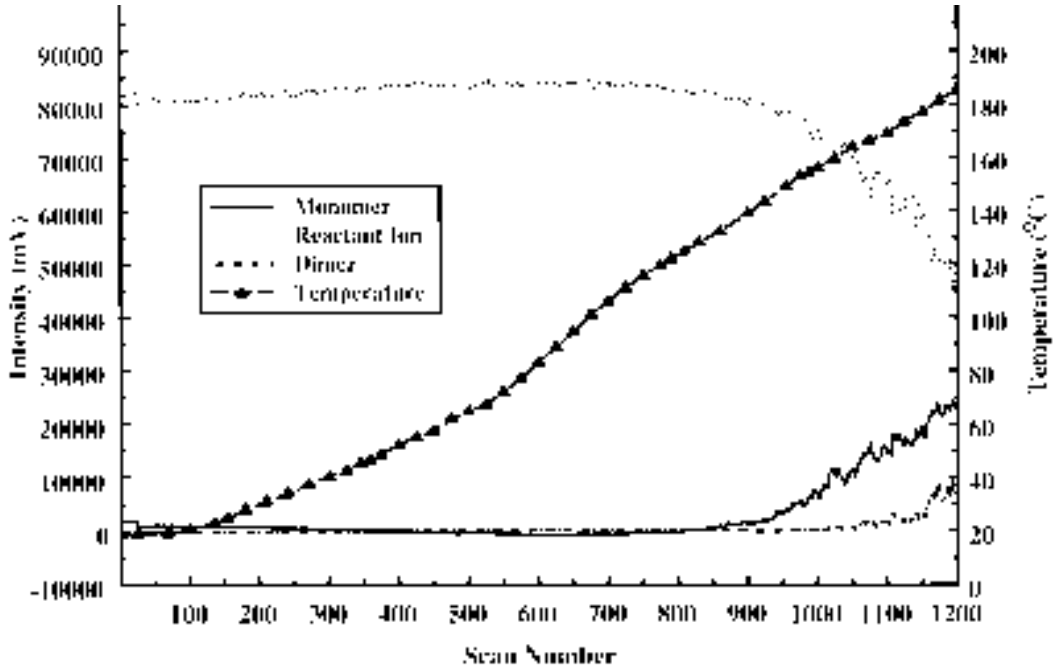


FIG. 2*a*—*SIMPLISMA extracted concentration profiles for methamphetamine hydrochloride with temperature profile. Components are ordered by purity and scan number refers to individual spectra.*

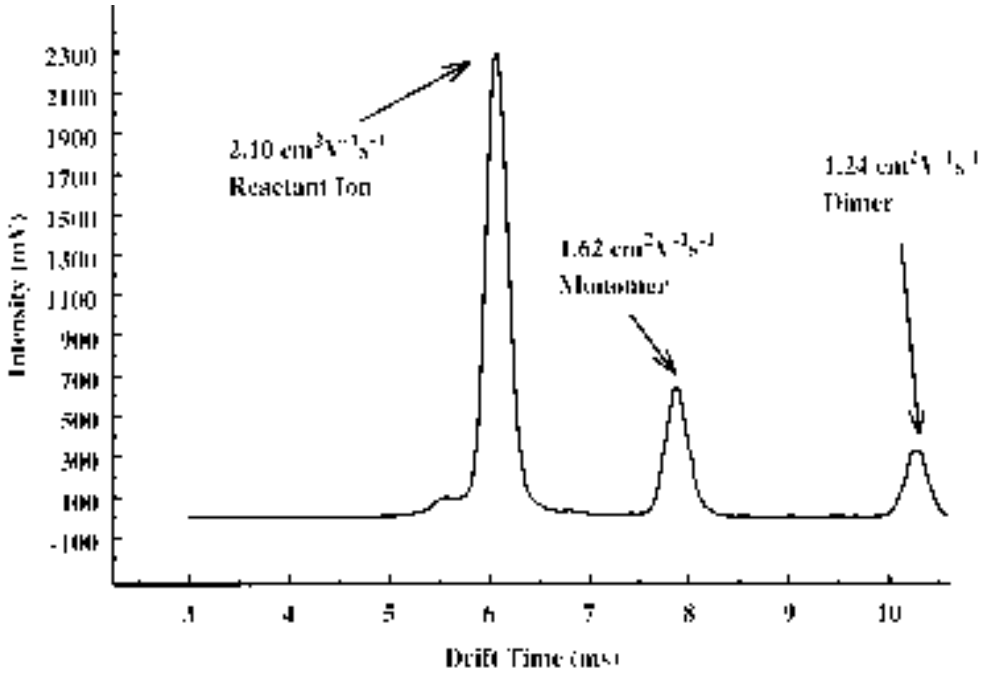


FIG. 2*b*—*SIMPLISMA extracted spectra from methamphetamine hydrochloride positive ion spectra. Components are ordered by SIMPLISMA purity value.*

instrument. Due to the effect of entropy, dimers are usually not observed at the higher temperatures. However, the peak identities reported in this paper should be considered tentative, until they are identified with an analytical tool, such as IMS/MS.

SIMPLISMA factors the data matrix into two matrices that can be viewed with simple 2D plots. The first matrix represents the change in concentration of mixture components with respect to time or temperature. This matrix is typically graphed (see Fig. 2*a*) as a function of intensity with respect to spectrum number. The columns of this matrix are referred to as concentration profiles, although they indicate relative concentrations in reproducing the data matrix and do not convey true concentration units. Each component represents a set of scaling factors as a function of scan number. For a given spectrum or scan number, these scaling factors can be applied to the corresponding extracted spectra (see Fig. 2*b*). The sum of the scaled spectra estimates the spectrum in the data at the given scan number. The advantage of SIMPLISMA is that the three-dimensional graph can be represented as too easy to interpret 2-D graphs.

By comparing Fig. 1 with Figs. 2*a* and 2*b*,, the benefits of SIMPLISMA may be seen. The components that are extracted are ordered by purity or importance. In Fig. 2*a*, the methamphetamine monomer component had a greater relative deviation so that it was modeled first by SIMPLISMA. The reactant ion decreases as the temperature increases, due to competitive charge transfer with the methamphetamine hydrochloride peaks. The temperature is the measured temperature of the beaker that contains the sample. As the methamphetamine hydrochloride vapor concentration increases a dimer peak begins to appear. The different rate of peak formation can be observed easily in Fig. 2*a* as opposed to Fig. 1*a*.

A typical cigarette smoke spectrum is given in Fig. 3*a*. SIMPLISMA was applied to a set of temperature program data acquired from 1 mg of cigarette tobacco residue. The concentration profiles and spectra from this data are given in Fig. 3*b* and 3*c*. Cigarette smoke peaks increase concomitantly with the increase in temperature. Broad peaks typify complex mixtures of volatiles that are sampled by the instrument. The signals attributed to smoke range in drift times from approximately 6.5 ms to 8.5 ms. Two maxima appear at 6.6 ms and 8.0 ms and their reduced mobilities were calculated. The peaks have reduced mobilities of 1.85 $cm^2V^{-1}s^{-1}$ and 1.56 $cm^2V^{-1}s^{-1}$, respectively. See Table 1. The peak at 8.0 ms has a reduced mobility that is consistent with the reported reduced mobility for nicotine (1). With such broad peaks, cigarette tobacco residue causes false positives and interferes with drug detection. SIMPLISMA may resolve the drug peaks from the interfering cigarette tobacco peaks. In addition to the reactant ion, two distinct components evolved as the temperature was increased. These components are labeled smoke peak 1 and smoke peak 2 in Fig. 3*b* and 3*c*. The reactant ion was extracted first by SIMPLISMA and represented as component 1 in these figures. Smoke component 1 may be a specific compound, while smoke component 2 appears to contain a mixture of less volatile compounds.

In a mixture of smoke tar and methamphetamine hydrochloride, the spectra become increasingly complex as the temperature is increased. SIMPLISMA was used to resolve the spectra into components that resolve characteristic features of methamphetamine hydrochloride. Figs. 4*a* and 4*b* are, respectively, the SIMPLISMA concentration profiles and extracted spectra. Upon comparison with the peaks in Fig. 2*b* and 3*b*, three peaks in Fig. 4*b* have similar extracted drift times. One peak (6 ms) is the reactant ion, and the other two peaks are consistent with methamphetamine hydrochloride. These peaks are labeled as monomer and dimer in Fig. 4*b*, although one cannot be sure as to their true chemical identities without further analysis. The peaks at 7 ms and 8.25 ms belong to component 3. This component represents the cigarette smoke residue. The peaks in this experiment have been shifted to later drift times (including the reactant ion peak) from the smoke standard run in Fig. 3*b*. The smoke peak component increases first in Fig. 3*a* and dominates the other peaks until a temperature of 170°C is achieved. Both components 2 and 4, have artifact peaks that arise from the cigarette smoke. The monomer component has an additional peak at 9.5 ms and the dimer peak has a shoulder with a small band. These peaks may arise due to the formation of mixed cluster ions between compounds in the smoke and the methamphetamine via the reaction given in Eq. 4.

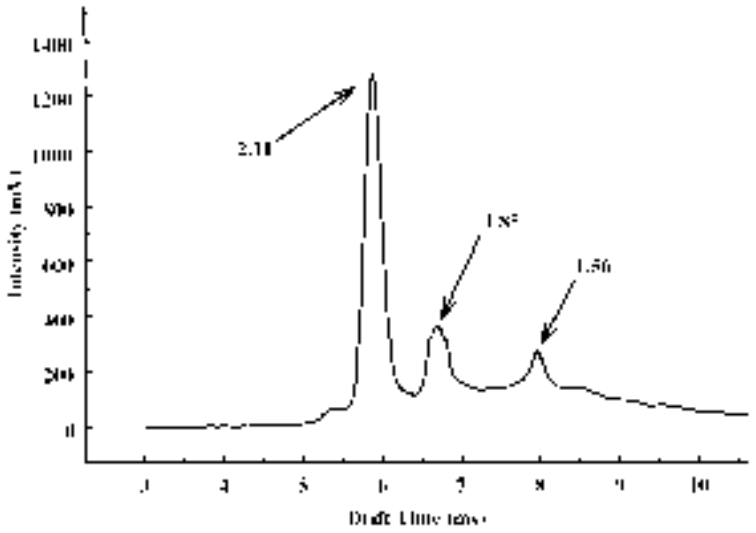
The handheld CAM combined with a laptop computer may provide a method for accurate screening of methamphetamine hydrochloride in the presence of interfering cigarette tobacco residues. Portable sample heaters may be developed to facilitate a rapid screen method that would allow a real-time scan of solid surfaces. The hand-held feature of the CAM may allow a more representative area of the crime scene to be surveyed. At higher temperatures (140 to 200°C), spectral features of methamphetamine become evident with the CAM. However, interferences such as smoke residue are also present in greater quantities confounding analyte features. With SIMPLISMA, the interfering signal may be separated from the analytical signal.

SIMPLISMA allows the detection of IMS features that would normally be missed by visual examination of IMS spectra. Because SIMPLISMA takes advantage of changes that occur in the spectral features with respect to time, the method is well suited for instrumentation that uses temperature programs for sample volatilization and decomposition. The concentration profiles provide valuable information regarding the changes in extracted spectral features with time or temperature. Although the APCI chemistry for IMS is complex due to the formation of heterogeneous ions, volatility provides an extra dimension that allows the resolution of mixture components. Furthermore, the complementary nature of the spectral and concentration profiles allows trends in the entire data set to be visually assessed. In addition, the storage of extracted spectra and concentration profiles is an efficient method of compressing large IMS sets of data.

This work presents a preliminary study that demonstrates the benefits of combining chemometrics with temperature programmed IMS data for screening drug samples. The temperature profiles may prove useful for identification of mixture components. The use of drift tubes at ambient temperatures also allows the detection of dimer ions. These ions may provide additional information that can be used to detect analytes when the monomeric peaks are obscured by interferents. Future work will evaluate this methodology on a modified Barringer Ionscan 350. This project will use precise temperature control and seek to minimize heating time and analysis time. Another project for future work is the identification of the IMS peaks caused by thermal desorption with an IMS/MS/MS system. Finally, the coupling of a heat source with a handheld IMS may provide an instrument that allows rapid scanning of crime scenes.

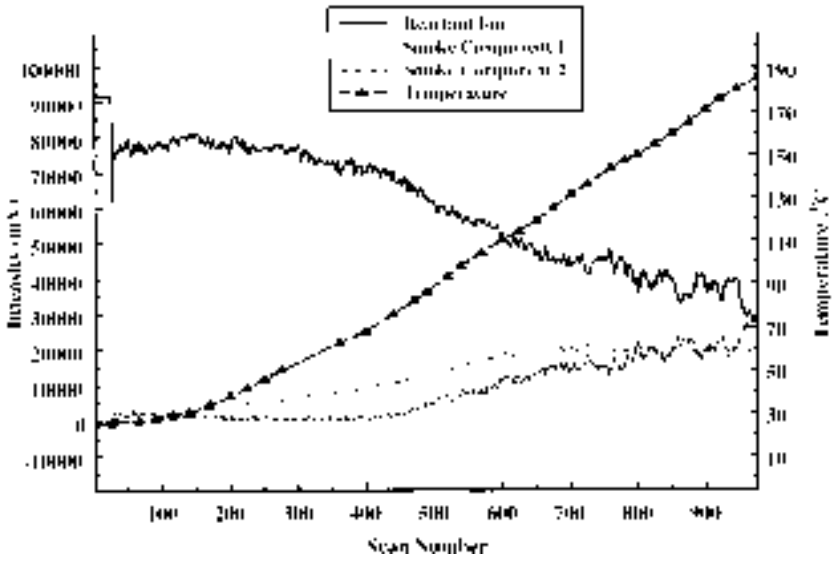
Acknowledgments

We would like to thank Willem Windig for his help with the SIMPLISMA algorithm. The U.S. Army ERDEC is thanked for their support of this research under contract DAAM01–95-C-0042. The authors would like to thank Ronald C. Tucceri, Paul J. Rauch, Tricia Buxton, Susan Slasel, James Y. Tong, Dennis M. Davis,



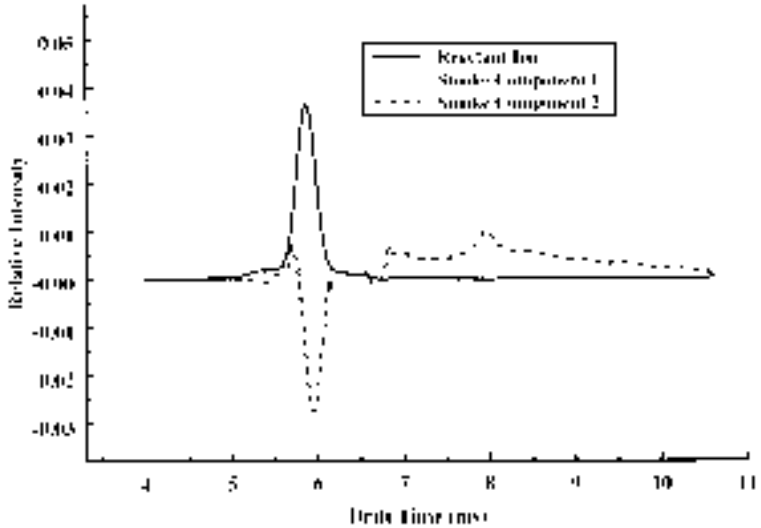
A

FIG. 3*a*—*Positive ion spectrum of cigarette smoke tar residue at scan number 975, collected at a temperature of 186°C.*



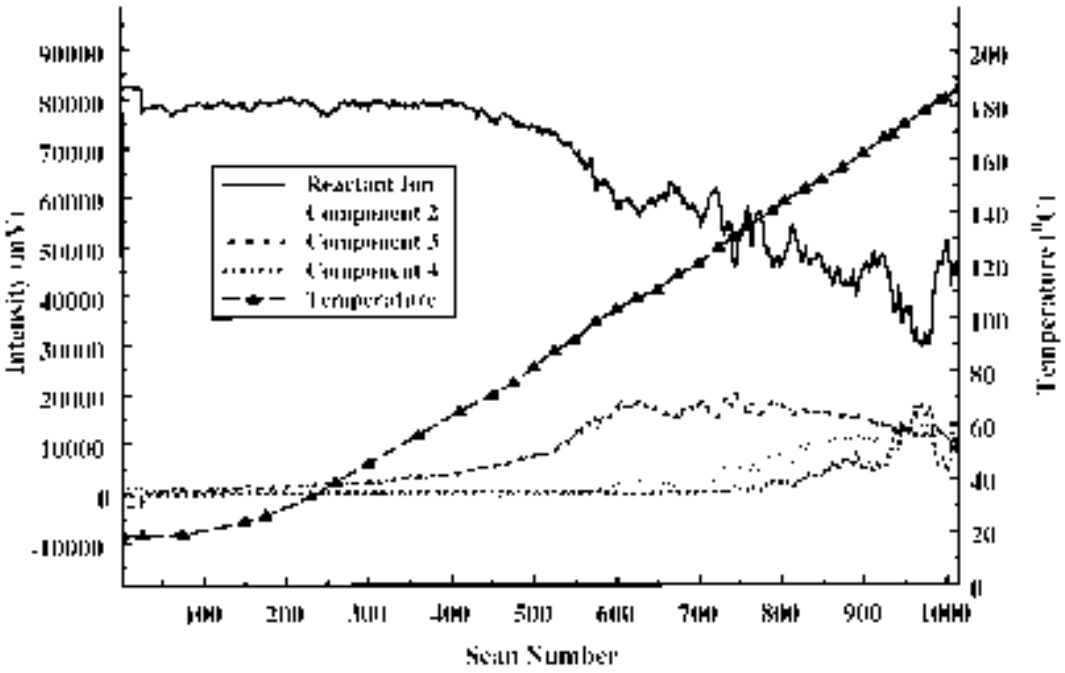
B

FIG. 3*b*—*SIMPLISMA extracted concentration profiles for cigarette smoke residue with the temperature profile.*



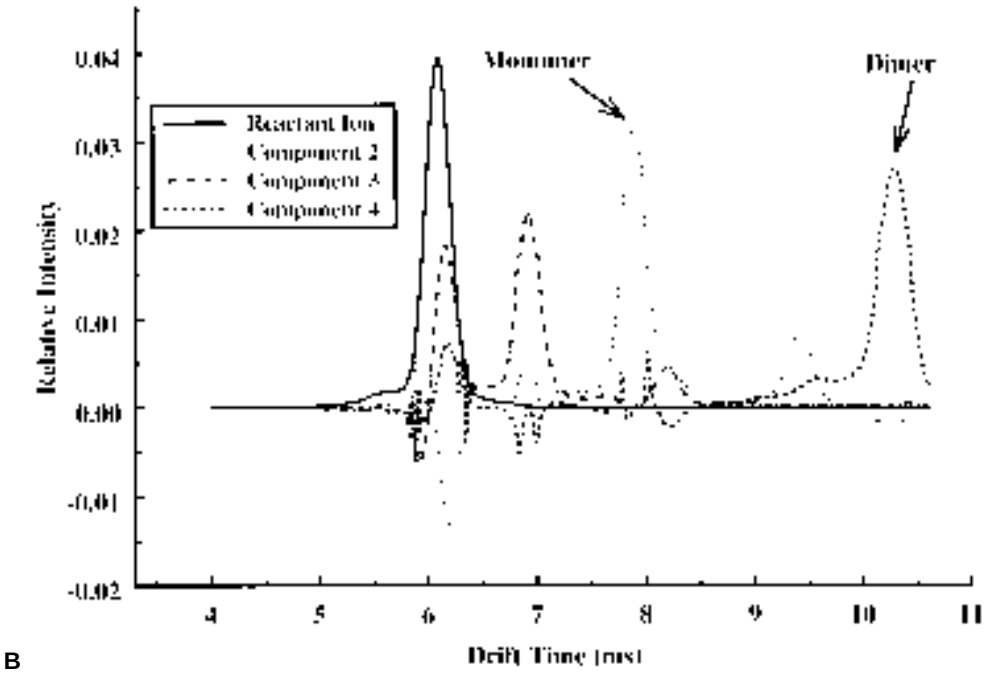
C

FIG. 3*c*—*SIMPLISMA extracted spectra from cigarette smoke residue and positive ion mobility data.*



A

FIG. 4*a*—*SIMPLISMA extracted concentration profiles for methamphetamine hydrochloride and cigarette smoke tar mixture with temperature profile.*



B

FIG. 4*b*—*SIMPLISMA extracted spectra for methamphetamine hydrochloride and smoke tar mixture.*

and Dewey King for their contributions to this work. The Federal Aviation Administration is thanked for the loan of the Barringer Ionscan® 350. The reviewers are thanked for their guidance and helpful comments.

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