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# MONITORING INDOOR AMBIENT ATMOSPHERES FOR VOLATILE ORGANIC COMPOUNDS USING AN ION MOBILITY ANALYZER ARRAY WITH SELECTIVE CHEMICAL IONIZATION

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Three ion mobility analyzers with different reagent gases for chemical ionization were interfaced to a single computer and operated with a software package created for simultaneous and continuous monitoring of 1 to 8 analyzers. Mobility spectra were collected and digitized on separate input channels with 200 ms sampling intervals for individual analyzers. Volatile organic compounds (VOCs) in indoor ambient atmospheres were monitored in two scenarios: laboratory air during designed releases of several VOCs and ambient air in a central chemistry storeroom used for undergraduate laboratories. The ion mobility analyzer with reagent ions of  $H(H_2O)_n^{*}$  (n = 2 - 4) exhibited response toward alcohols, aldehydes, and other VOCs with low proton affinities. However, analyzers with reagent ions of elevated proton affinity including acetone and dimethylsulfoxide showed selective response toward only VOCs with proton affinities greater than that of the reagent ion. Thus, two tiers in selectivity of array response were established through the ionization chemistry joined with ion mobilities and was demonstrated through studies of indoor air quality.

**KEY WORDS:** Ion mobility spectrometry (IMS), analyzer array, selective chemical ionization, ambient atmosphere, monitoring, volatile organic compounds.

## INTRODUCTION

Ion mobility spectrometry (IMS) is an instrumental technique for the characterization of molecules based upon gas phase mobilities of ions in air at atmospheric pressure and in a weak electric field<sup>1</sup>. Although modern analytical IMS is over two decades old, the technique recently has received renewed attention<sup>2,3</sup> with advances in knowledge of operating principles, refinements in instrumentation, and improvements in the practice of IMS. This renewed interest has occurred from the advantages of ion mobility analyzers in regard to size, weight and power for portable field instruments<sup>4</sup>. In IMS, vapors are drawn into a reaction region where constituents of the sample are ionized through atmospheric pressure chemical ionization (APCI) reactions. These ions are then characterized in a drift region through measurement of ion velocities. Ion speeds are related principally to collision cross sections and ion separations are based upon size to

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charge ( $\Omega/z$ ) ratios. Ions pass through the drift region of hand-held IMS analyzers in 6 to 15 ms and ion characterizations occur repetitively at roughly 30 Hz. Analytical information is obtained as the mobility spectrum or detector response versus ion velocity, or drift time, and mobility spectra can be used for identifying vapors.

Limitations with the current generation of drift tubes for IMS include low resolution for ion separations and preferential response from competitive charge distribution during the formation of ions. Thus, direct analyses of mixtures can be complicated and approaches to this limitation have included: the construction of large, high voltage drift tubes that exhibit high resolution<sup>5</sup>, the use of alternate reagent ion chemistry to offer an additional dimension of selectivity through APCI reactions<sup>6,7</sup>, and the prefractionation of sample with a gas chromatograph inlet<sup>8</sup>. Contemporary high resolution drift tubes are impractical for field applications but the other approaches have been successfully applied in portable environmental analyzers.

Ion mobility spectrometers have also been used for atmospheric monitoring of organic vapors under conditions when a single vapor existed in air free of potential intereferences. However, in the monitoring of air containing possibly complex mixtures of volatile organic compounds (VOCs), the low resolution of mobility spectra may diminish the reliability of response. An alternative to the technical solutions cited above lies in the opposite extreme where miniaturized ion mobility sensors with truncated resolution are used in arrays<sup>9</sup>. Selectivity in response in such arrays was controlled largely through the chemistry of APCI reactions. Reagent gases that are intentionally added to the ion source can impart APCI specificity by excluding response to molecules with proton affinities below those of the reagent gas. This idea might be particularly effective if arrays of ion mobility sensors, each with a unique reagent gas, would be used in a single location. Thus, the merger of ionization selectivity with multiple point analyzers could provide enhanced confidence in atmospheric monitoring over the response of a single analyzer alone. This has been a motivation for the development of IMS sensors' and in this report, the chemical principles to accomplish such sensor arrays are demonstrated for indoor atmospheric monitoring.

Formation of ions is the first molecular event in IMS and is the principal factor in controlling response of IMS analyzers or sensors. Vapors will be ionized when the proton affinity (PA) of the analyte vapor (A) is greater than the PA of the charge reservoir (i.e. the reactant ions) per equation 1:

$$A + (H_2O)_n H^* \longrightarrow A \cdot H^* + nH_2O$$
(1)  
Analyte Reactant Ion Product Ion

The major reactant ions in air or nitrogen, at atmospheric pressure in positive polarity, are hydrated protons which have comparatively low proton affinities and will therefore react indiscriminately with most VOCs via proton transfer reactions (eq. 1). However, the intentional addition of a vapor (B) to the ion source under continuous and uniform conditions will result in the formation of alternate reactant ions per equation 2:

$$B + (H_2O)_n H^* \longrightarrow B \cdot H^* + nH_2O$$
Reagent Reactant Ion Alternate
Reactant Ion
(2)

Should the PA of an analyte exceed that of the alternate reactant ion  $(B \cdot H^{+})$ , ionization can occur through collisional proton transfer reactions per equation 3:

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$$\begin{array}{ccc}
A & + & B \cdot H^{*} & - - - \bullet & A \cdot H^{*} & + & B \\
Analyte & Alternate & Product Ion \\
Reactant Ion & & & & \\
\end{array}$$
(3)

However, if the PA of the analyte vapor is lower than that of the alternate reactant ion, product ions for the analyte will not form and the reactant ion peak (RIP) in the mobility spectrum will be unchanged. If other compounds are also present, they will compete for the available charge (the protons in this case), and the charge will be distributed among these according to relative PA and vapor concentrations. Thus, ion source chemistry in IMS may be designed to establish selectivity through control of the ionization step for product ions formation.

Three successful examples of applications of alternate reagent ion chemistry include IMS detection of chemical warfare agents<sup>10</sup>, hydrazine fuels<sup>7</sup>, and acid gases<sup>11</sup>. In the present work, an IMS monitoring array is described with simultaneous operation of three IMS analyzers (but with an option for as many as eight) based on different reagent gas chemistry. Performance of the array including software was evaluated through two monitoring scenarios: a set of designed releases of vapors and an actual indoor air quality study. The goal for this work was to ascertain the value of IMS analyzer arrays with selective chemical ionization in air monitoring applications.

## **EXPERIMENTAL**

#### Instrumentation

Three hand-held ion mobility analyzers used here were Chemical Agent Monitors (CAM) or civilian versions of CAM made by Graseby Dynamics, Ltd. (Watford, Herts., UK) and have been described previously<sup>10</sup>. The drift tube consists of a 10 mCi <sup>63</sup>Ni ion source and a 38 mm long by 11.5 mm diameter drift region with an average field gradient of 215 V/cm. Each analyzer had an internal pneumatic system enabling ambient air to be sampled at a rate of 0.5 L/min. The analyzer drift tube was isolated from the ambient air though a thin polymethylsilicone membrane, used to maintain stable levels of moisture in the drift tube. Also in this flow system, air drift gas was re-circulated at ca. 200 mL/min in the drift tube and was purified before reuse through scrubbers containing 13X (8–12 mesh) molecular sieve.

An IBM-PC compatible computer was used to acquire, manipulate, display and store mobility spectra from each IMS analyzer. The computer was equipped with a model DT2812 analog-to-digital conversion (ADC) board, a model DT717 terminal panel, and a model EP227 cable (Data Translation, Inc., Marlboro, MA). This assembly allowed sampling of 1 to 8 IMS analyzers using a single computer. A signal and synchronization line were connected into the distribution board for each IMS analyzer.

Ion identifications were made using an IMS/MS/MS modified from an atmospheric pressure chemical ionization tandem quadrupole mass spectrometer, model TAGA 6000 (Sciex, Inc., Toronto, Ontario, Canada). Retaining plates and the vacuum chamber gate valve were removed from the source end of the TAGA 6000 vacuum housing to allow close access to the pinhole interface. Voltage of this interface was reduced to ca. 200 volts and an IMS drift tube, identical to those used in the CAM instruments, was positioned within 2 mm of the pinhole interface. Other parameters have been reported<sup>7</sup>. Collision induced dissociation was used to fragment selected ion clusters for identification or structure assignment.

## Software

A customized software package was written to support the Data Translation ADC board and to sample signal from 1 to 8 IMS analyzers. Special attention was given to an alarm system where the intensity of the reactant ion peak (RIP) was used as the main indicator of air quality or cleanliness of total airborne vapors. Although RIP intensities were stored continuously, mobility spectra were stored only when a threshold level for RIP intensity was toggled. In Figure 1, a schematic flow chart of the operations and logic of the program are depicted. Preliminary steps include initializing the interface board, performing a status check on each IMS analyzer, establishing direct memory access, and setting the sampling frequency. The software permitted both the section and control of individual analyzers and the presentation of information on a video-monitor. When acquisition of mobility spectra begins, results are stored in a buffer. The height of the



Figure 1 Flowchart for main routine in software for continuous monitoring of vapors using IMS analyzer array with a single computer.

RIP is calculated and compared with a stored (i.e. baseline) value. If the RIP intensity exceeds the stored maximum value (i.e. the RIP in a clean spectrum), the new value is stored replacing the old value. In one version for the video-monitor, dots representing analyzers in the array are color coded for prevalent RIP conditions. An analyzer with only baseline intensity for the RIP is shown as a green dot. The dot is changed to yellow and an audio alarm is given when the RIP intensity falls below a primary threshold. Decline of the RIP intensity below a secondary threshold causes a change in the audio alarm frequency and the dot is changed to red. In either instance, mobility spectra and clock time are stored when the primary threshold is exceeded and storage continues so long as the threshold condition is exceeded. After sequencing through all active IMS instruments, the next monitoring cycle begins.

Another video-monitor display includes the real time display, for an analyzer selected by the use, of individual mobility spectra and a record or trace of RIP intensity versus clock time from the start of a monitoring exercise. The height of the RIP is determined within a preset spectral window to generate the trace and a similar arrangement can be made to follow the product ion peak height in other preset spectral windows. A total cycle time for measurement of peak heights and storage of spectra, when necessary, for three IMS analyzers was set for every 60 sec. A example of one video-monitor display is shown in Figure 2 for the RIP trace (top frame) and for the mobility spectrum (bottom



**Figure 2** Video-monitor display of reactant ion peak intensity versus clock (upper frame) during an vapor exposure episode at approximately 2:30 PM to 3:30 PM. In the lower frame, a stored mobility spectrum is displayed from the archive file at 2:44 PM (note position of cursor in upper frame). The peak on the left is at 6.7 ms is the reactant ion peak (RIP) for DMSO reagent gas and the peak on the right at 7.2 ms is the product ion for 2,4-lutidine.

frame). Spectra can be displayed in real-time, or from archived data using a cursor.

The weighting algorithm – The rate at which mobility spectra are acquired depends on the sampling frequency set by the operator. A sampling frequency of 60 kHz was selected for digitizing data. In addition, the signal-to-noise ratio can be improved in IMS through averaging of several mobility spectra before displaying and processing them. The algorithm used here is based on an exponential filter and is biased in favor of the latest acquired spectra as triggered by a drop in the RIP intensity below a threshold. The displayed spectrum, SPEC<sub>n</sub>, is a composite of the last raw data spectrum, X<sub>n</sub>, and the previous one, X<sub>n-1</sub>, which has been processed by the filter per equation 4:

$$SPEC_{n} = (X_{n-1} + X_{n})/2$$
 (4)

where,

$$\mathbf{X}_{n-1} = (\mathbf{X}_1 + 2^1 \mathbf{X}_2 + 2^2 \mathbf{X}_3 + \dots 2^{n-1} \mathbf{X}_{n-1})/2^{n-1}$$
(5)

Thus, the action of the filter is to combine several spectra with proper weighting. An advantage of using this algorithm is that the processing required to average the latest spectrum is simple and fast as the calculation is based on equation 4. Use of this algorithm enables the system to monitor up to eight IMS analyzers and continuously refresh the display on the screen after each new spectrum is acquired, without waiting several seconds for new spectra to be acquired, digitized, averaged, stored, and display.

## Procedures

The two experiments that are described below include: A) a set of designed vapor exposures in a laboratory to verify performance of the IMS array and B) a monitoring exercise without prior knowledge of air quality or control of atmospheric vapors. In the laboratory studies, three hand-held IMS analyzers (i.e., CAMs) were operated with either water, acetone or DMSO reagent gases. In the second study, two CAMs were used with acetone reagent gas and a third CAM was operated on water reagent gas. Preliminary trials had demonstrated th absense of VOC vapors suitable to cause response on the DMSO-based CAM and a second acetone-based CAM was added as a measure of reproducibility.

## Designed laboratory studies

In these studies, three CAMs were connected to the monitoring system and operated in the positive ion mode. Studies were conducted during a work-day in a graduate research laboratory absent organic solvents in routine activities. A baseline data set for the RIP was collected from each analyzer for two hours of sampling. Then the analyzer array was exposed to acetone vapors for about 40 minutes using a diffusion source located in the laboratory 3 m from the array; then the acetone source was removed. Analyzers returned to baseline response or ion source cleanliness after approximately 90 minutes and then acetophenone was released, as above, for about 50 minutes. Based on results from prior calibrations of CAMs<sup>6,7</sup>, the response of the water-based CAM to either vapor in the laboratory atmosphere suggested vapor concentrations in the range of 0.1–1 ppm..However, vapor levels were not otherwise controlled or quantitatively

determined for these demonstrations. Finally, after another hour, the analyzer array was exposed to 2,4-lutidine (dimethylpyridine) vapors for 30 minutes. The intensity of the RIP was monitored throughout each test and spectra were stored when a sensitive RIP threshold was exceeded within individual analyzers.

#### Monitoring indoor atmosphere of a chemistry storeroom

The computer and IMS analyzers were moved to the chemical storeroom for the Department of Chemistry and Biochemistry at New Mexico State University where an extended monitoring exercise was conducted. Ambient atmosphere was monitored from 9 AM to 5 PM on consecutive days for three days and overnight for two nights. On two days, freshman chemistry laboratories were in operation and on one day, these classes were supplemented with two organic chemistry classes.

## **RESULTS AND DISCUSSION**

### Designed laboratory studies

Results from monitoring of the designed release of organic vapors in the laboratory for the IMS analyzer with water reagent gas (i.e. unselective response) are shown in Figure 3A as a plot of RIP intensity versus clock time. The early portion of the trace, to approximately 10 AM, exhibited stable response without significant changes in intensity until acetone vapors were released in the laboratory atmosphere at 10:15 AM; intensity of the RIP decreased rapidly and stayed relatively constant and low until the vapor source was removed. Afterwards, the RIP intensity returned to the original baseline intensity as acetone vapors in the ambient atmosphere were diluted by fresh air from the ventilation system of the building. Clearance of vapors from CAM type IMS analyzers after a vapor exposure occurs on the time scale of 2–10 minutes<sup>6</sup> suggesting that the principle cause for the rate of restoration to baseline in Figure 3A was the diffusion and dilution of vapors in the atmosphere and not instrument hysteresis. Response for analyzers with acetone reagent gas and with DMSO reagent gas are shown in Figures 3B and 3C, respectively; for the same air containing acetone, virtually no response was observed on either of these two analyzers between 10:15 to 11:00 AM. This behavior was consistent with the competition for charge between the PA of the analyte acetone at 196.7 kcal/mole and PA for the reagent gases of water at 166.5 kcal/mole, acetone, and DMSO at 211.3 kcal/mole.

At 12:45 PM, vapors of acetophenone (PA=205.4 kcal/mole) were released at three meters distance from the analyzer array and response was observed in two IMS analyzers, those with water or acetone reagent gases. The proton affinity of acetophenone was greater than those for either of these reagent gases but not greater than that for DMSO. Consequently, response to the acetophenone was not observed in the third IMS containing DMSO reagent gas. Although the comparative responses of the analyzers to acetophenone differed, the significance of such differences was unknown in the absence of detailed calibrations not made for these studies. As with the exposure to acetone vapor, response to acetophenone diminished when the diffusion source was physically removed from the laboratory at roughly 1:30 PM (1330 hr in Figure 3) and baseline cleanliness was restored in each IMS analyzer.

Response to 2,4-lutidine (released at 1420 hrs per Figure 3) was evident in each of the





Figure 3 Plots of RIP intensity versus clock time for three IMS analyzers with different reagent ion chemistry during the designed releases of vapors into laboratory air. Traces corresponded to response from IMS analyzers containg reagent gases of A. water, B. acetone, and C. DMSO. All of the three IMS analyzers were exposed to acetone, acetophenone and 2,4-lutidine for 30–50 minutes at 10:15 AM, 12:45 PM, and 2:20 PM, respectively.

IMS analyzers as anticipated from the high PA (227.3 kcal/mole) of 2,4-lutidine. It should be noted that in the DMSO-based instrument the reactant ion peak and product ion peak from 2,4-lutidine were separated only by about 0.5–0.6 ms (see lower frame of Figure 2 where the RIP and product ion appear at 6.6 and 7.2 ms, respectively) and some overlap of peaks occurred at high concentrations of 2,4-lutidine vapors. Thus, the monitored decrease in the RIP intensity, shown in Figure 3, did not accurately reflect the actual reduction in RIP intensity.

One option in the software is to obtain, view and store ion mobility spectra corresponding to the decline in RIP intensity. The RIP trace from the monitoring exercise for water and acetone reagent gases showed serious decline in the RIP intensity during exposures to acetophenone and 2,4-lutidine (Figure 3A and 3B). Ion mobility spectra corresponding to these two exposure events with acetone reagent gas are shown in Figure 4 for acetophenone (upper trace) and 2,4-lutidine (lower trace). The product ions appear at drift time greater than that for the RIP which in both spectra was the dimer ion  $Ac_2$ ·H<sup>+ 10</sup> at a drift time of 6.3 ms. Although the drift scale is compressed in the frames shown in Figure 4, drift times for the product ions were different and were larger than that for the RIP. Mobility spectra reflect the identity of ions created from a vapor through APCI reactions. In this instance, the identities and drift times for the product ions of acetophenone were a monomer ion, M·H<sup>+</sup>, at 7.6 ms and a dimer ion, M<sub>2</sub>·H<sup>+</sup>, at 8.8 ms while those for 2,4-lutidine were M·H<sup>+</sup> (7.3 ms) and M<sub>2</sub>·H<sup>+</sup> (8.2 ms). These ion identities were confirmed using IMS/MS as shown in Figures 5 and 6. In Figure 5A, the



Figure 4 Mobility spectra obtained for acetophenone (upper trace) and 2,4-lutidine (lower trace) with an IMS analyzer containing acetone reagent gas.

mass spectrum is shown from MS determination of all the ions inside the IMS with acetone reagent gas. The predominant ion species is  $Ac_2$ ·H<sup>+</sup> or the dimer ion at m/z 117. Small amounts of hydrated dimer ion are evident at m/z 135 and small amounts of M·H<sup>+</sup> (m/z 59) and hydrated M·H<sup>+</sup> (m/z 77) are also visible. Vapors of acetophenone exhibited proton transfer reactions principally to M·H<sup>+</sup> (m/z 121) and M<sub>2</sub>·H<sup>+</sup> (m/z 241) as shown in Figure 5B. Another dominant peak at m/z 179, as shown in Figure 5B, could be the adduct ion [acetone-acetophenone·H<sup>+</sup>]. Reactions by APCI of 2,4-lutidine with Ac<sub>2</sub>·H<sup>+</sup> showed M·H<sup>+</sup> (m/z 108) at low concentrations (Figure 6A) and M<sub>2</sub>·H<sup>+</sup> (m/z 215) at elevated concentrations (Figure 6B). The m/z 166 in the mass spectrum of low concentrations for 2,4-lutidine (Figure 6A) could be derived from [lutidine-acetone·H<sup>+</sup>] adduct ions. Collision induced dissociation results (not shown) supported the identification of these cluster ions. At the conclusion of this set of designed vapor release studies in the laboratory, the software and performance of the IMS array was considered sufficiently reliable for a monitoring exercise with actual indoor ambient atmospheres.

## Monitoring indoor atmosphere of a chemistry storeroom

An example of an industrial hygiene situation in close proximity to the laboratory was the chemistry stockroom which serves as a central store of chemicals, solvents, laboratory equipment, and materials for undergraduate laboratories. These laboratories are operated afternoons on weekdays and since prior reports of odors existed, the IMS array was relocated to the chemistry stockroom for continuous atmospheric monitoring. On two days of monitoring in the morning and afternoon, the RIP trace from the waterbased CAM or acetone-based CAM showed no detectable amounts of VOCs at estimated



Figure 5 Mass spectra from IMS/MS characterization of (A) acetone reagent gas alone and (B) acetone reagent gas with vapors of acetophenone.

detection levels of 50–100 ppb. During these days, freshman chemistry laboratories were convened and these laboratories involved little or no use of organic solvents. Notably different results were obtained on a day during which organic laboratories also were in operation as shown in Figure 7. In the top frame Figure 7, RIP intensity plots are shown for IMS analyzers with acetone (upper trace) and water (lower trace) reagent gases. The response in the upper trace for the acetone reagent gas suggested the absence of VOCs with proton affinities above that of acetone (see Table 1) during both morning or



Figure 6 Mass spectra from IMS/MS characterization of (A) 2,4-lutidine at low vapor concentrations and (B) elevated vapor concentrations. In both measurements, acetone was the reagent gas.

afternoon. However, the RIP record for the water-based IMS analyzer (top frame, lower trace), showed a relatively clean atmosphere until the start of laboratories, including the organic chemistry laboratories at 2 PM. The decline in RIP intensity suggested the presence of VOCs with proton affinities below that for acetone but above that for water. Representative organic chemicals are shown in Table 1 solely to illustrate the possible types of chemicals. Proton affinities suggested by these results are typical of alcohols, esters, or aldehydes. The presence of these solvents in the indoor atmosphere of the stockroom was coincident with the activities of students who would come to the



Figure 7 Intensity for the RIP versus clock (top frame) during the morning and afternoon when laboratory were active using IMS analyzers based on acetone reagent gas (upper trace) and water reagent gas (lower trace). In the bottom frame, the mobility spectrum is shown from the ion mobility spectrometer with water reagent gas at the cursor location shown in top frame, lower trace.

stockroom to obtain solvents and samples. This was in agreement with the reported use that day of organic solvents including alcohols and esters. In the bottom frame of Figure 7, the ion mobility spectrum obtained from the water-based IMS during the organic chemistry laboratory classes is shown and several product ion peaks are evident in the spectrum. The drift times of these product ions are consistent with low molecular weight (2 to 6 carbon number) alcohols and esters though no further attempt was made here to trap and identify the solvent vapors. Comparison of two acetone based CAMs showed good agreement as expected for CAMs where reproducibility error is 5-10% for long-term stability<sup>7</sup>.

Previous monitoring of the stockroom for two days showed no obvious changes in RIP intensity with one exception. The ambient air during the general chemistry classes is free of organic solvents and mainly mineral acids, such as hydrochloric acid and sulfuric acid with proton affinities below that of water, are used. However, a strong response was observed with every analyzer and a product ion peak appeared at a drift time shorter than that for the RIP. The drift time for this ion in a CAM was known previously and reproduced with authentic standard as ammonia and the ion was identified with IMS/MS as  $NH_4^+$ . This peak was observed when ammonium hydroxide (PA for  $NH_3$  =

#### VOC's IN INDOOR ATMOSPHERES

PA**	Chemical
232.2	Triethylamine
226.4	Piperidine
220.8	Pyridine
214.1	Methylamine
211.3	DMSO
205.0	Diethylsulfide
204.0	Ammonia
201.4	Cyclohexanone
200.2	Diethylether
198.8	Tetrahydrofuran
197.8	Methyl acetate
196.7	Acetone
193.8	Dioxane
193.2	Nitrobenzene
192.0	p-Xylene
191.2	Isopropanol
190.2	Acetic Acid
188.2	Acetonitrile
181.9	Methanol
181.3	Benzene
178.8	Formic Acid
169.0	Cyclohexane
166.5	Water
164.4	Carbon Disulfide
150.1	Propane
131.4	Methane
128.6	HCI

Table 1 Proton Affinities\* of representative chemicals

\* Proton affinity is defined as the negative  $\Delta H$  for the reaction HB  $\Rightarrow$  H<sup>\*</sup> + B.

\*\* Proton affinity units are kcal/mole. Taken from reference 12.

204.0 kcal/mole) was distributed to the students and the peak gradually diminished as vapors of ammonia were dissipated.

## CONCLUSIONS

A monitoring system based on an array of IMS analyzers with controlled chemical ionization was proven in principle and operation through laboratory studies. An approach to specificity of response with two tiers of selectivity was demonstrated from releases of selected volatile organic compounds and the comparison of response by IMS analyzers with reagent gases of different proton affinities alone was demonstrated as effective in a general classification of chemical vapors. Additional selectivity involving drift times for product ions was evident but not exploited in these studies. Further selectivity from drift times and the use of negative polarity response should make IMS analyzers alone may yield indeterminate or confusing response. Thus, further developments for IMS sensors<sup>9</sup> such as those achieved for electrochemical arrays<sup>13</sup> may prove advantageous providing sensors and signal processing are fully integrated.

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