Tunable Selective Detection for Capillary Gas Chromatography by Ion Mobility Monitoring

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An ion mobility spectrometer (IMS) has been constructed specifically for interfacing with gas chromatography. Modifications to standard designs include (1) a unidirectional gas flow, (2) an enclosed drift tube, (3) a reduced ionization cell volume, and (4) introduction of samples between the ionization region and the first ion gate. The purpose of each of these novel modifications was to reduce the loss of chromatographic resolution in the detector by increasing the efficiency with which neutral sample species are removed from the ionization region. By use of repetitive injections of a gasoline sample, separated on a fused silica capillary column, a nonselective negative peak detection mode, a nonselective positive peak detection mode, and several selective mobility monitoring modes were investigated. With selective mobility monitoring the responses of xylenes in one mode and substituted naphthalenes in another mode illustrate the operation of the IMS as a tunable selective detector.

In ion mobility spectrometry (IMS), ions with varying velocities are separated in space as they travel through an inert gas in an electric field at atmospheric pressure. Characteristic ions provide an ion mobility spectrum of the substance ionized which can be converted to both quantitative and qualitative information. Despite the potential of IMS in chemical analysis, its only application has been as a technique known as plasma chromatography (PLC) in which the ionization source is similar to that employed in an electron capture detector and the sample chamber is designed for the continuous introduction of organic compounds of high purity. A more complete description of the theory of ion mobility spectrometry has been provided by Revercomb and Mason (*1*).

The principal advantage of IMS in chemical analysis is that it can serve as an extremely sensitive detection method for organic compounds. Although modes of operation are similar to that of low-resolution mass spectrometers, ion mobility spectrometers separate ions according to their mobilities at atmospheric pressure instead of mass to charge ratio of the ion. (It is possible in some cases for ions of the same mobility to have different masses.) As in the analysis of organic mixtures by mass spectrometry, IMS should be most effective when each compound is introduced independently after separation by gas chromatography.

The potential of IMS as a tunable selective detector for gas chromatography has been recognized since its introduction as an analytical method for trace organic analysis in 1970 by Cohen and Karasek (*2*). A number of articles, published by Karasek and co-workers (*3–5*) and others (*6–9*), demonstrated the advantages of ion mobility spectrometry as a GC detection method. However, the use of IMS as a GC detector has not been commonly employed due to two major technical problems. First, sensitivity of the method was so great that residual solvent, unseparated components, background bleed from the column, or contamination of the carrier gas changed, complicated, or completely eliminated response. Second, cell volumes of commercially available instruments were so large that diffusion and adsorption effects caused serious loss of quantitative reproducibility, sensitivity, and chromatographic resolution. Recent developments such as permanently bonded monomolecular layer GC phases and fused silica capillary columns reduced interferences from column bleed, but detector design still rendered IMS impractical for use with high-resolution separations.

The objective of this work was to design a tunable selective detector based on the principles of ion mobility spectrometry specifically for use with capillary gas chromatography.

EXPERIMENTAL SECTION

Design of Detector. The ion mobility spectrometer designed for this project is shown in Figure 1. The ion drift tube is constructed from a series of stacked stainless steel guard rings separated by glass insulator rings. Adjustable insulated tension bars hold the instrument together thus allowing alteration of the length and position of the ion separation region by addition or removal of stainless steel rings. (Separation region lengths of 4.8 and 7.5 cm were employed in these studies.) A high voltage (typically a positive 3000 V) is applied to the repeller plate of the detector. This voltage is dropped to ground via a series of 1-MΩ resistors (not shown in the figure) which are connected to each of the guard rings. Thus, an electrical field of about 200 V/cm is maintained down the tube. Clean, dry nitrogen is introduced at the base of the detector, flowing up the drift tube and exiting through the top plate. The GC effluent enters through an orifice located between the drift region and the ionization region. The ionization source of the detector consists of a 15-mCi ^{63}Ni foil (New England Nuclear, Boston, MA) similar to that employed in commercial electron capture detectors. Samples from the GC are swept through the ionization region and exit with the drift gas through the top plate. Since the cell volume of the ionization region is only 1 cm^3 and flow of the drift gas plus makeup and carrier gases from the GC is typically about 600 mL/min, the residence time of a sample in the ionization region is on the order of 0.1 s.

When positive ions are formed in the vicinity of the ^{63}Ni foil, they drift in the field toward the entrance gate where they are stopped from continuing down the tube by a 900 V/cm field which is applied orthogonal to the drift field. Under these conditions this first gate is said to be closed. At designated times this orthogonal field is removed for 0.2 ms, opening the gate and allowing a pulse of ions to pass into the ion separation region. Ions that are admitted to the separation region continue to migrate down the tube at different mobilities, arriving at gate 2, the exit gate, at different times. If gate 2 is open when they arrive, the ions pass through and are collected at the electrode. If gate 2 is closed when they arrive, no detection occurs. Gate 2 can either be opened at progressively increasing intervals after gate 1 to produce an ion mobility spectrum or it can be opened at some fixed interval after gate 1 to monitor only ions of a certain mobility. Control of gates 1 and 2 is accomplished by an AIM 65 microcomputer (Rockwell International, Anaheim, CA). The third, or passive, gate is connected electrically to the surrounding guard ring. Its function is to prevent transient noise generated from the opening and closing of gate 2 from reaching the collector electrode. Operating conditions are summarized in Table I.

Capillary Gas Chromatography. A Tracor 560 capillary chromatograph (Tracor Instruments, Austin, TX) equipped with a split and splitless injector and a flame ionization detector was

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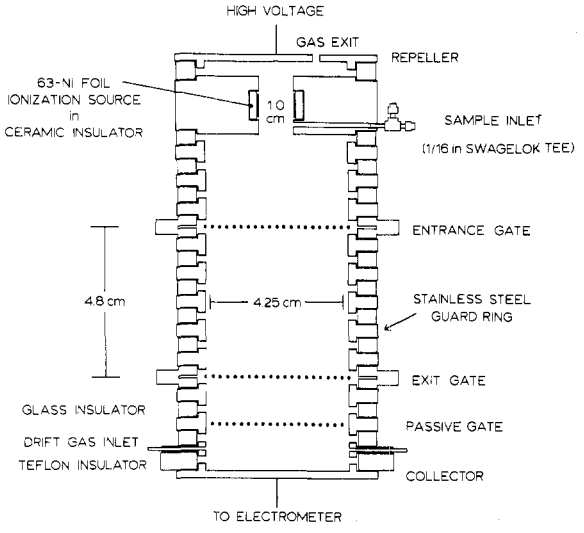

Figure 1. Schematic diagram of ion mobility spectrometer.

Table I. Operating Conditions

Ion Mobility Spectrometer	
ion drift length:	7.5 cm[a]
temperature:	140 °C
nitrogen drift gas flow rate:	600 mL/min
electric field gradient:	215 V/cm
chart speed:	0.5 cm/min
Chromatograph	
column:	15 m fused silica, SE-54 coated
flow rate:	0.5 mL/min (nitrogen)
split ratio:	50:1
injection port temperature:	200 °C
temperature program:	
initial temperature:	40 °C
ramp:	2 °C/min
final temperature:	100 °C
final hold:	10 min

[a] Ion drift length = 4.8 cm for the reduced mobility studies.

employed by using standard operating conditions recommended by the company. Separation was accomplished with an SE-54 fused silica capillary column (J and W Scientific, Inc., Rancho Cordova, CA) which either was connected to the FID of the Tracor instrument or was threaded through a heated 3 ft × $^1/_8$ in. o.d. copper transfer line into the IMS. Unleaded gasoline was chosen as a complex test sample to compare detection performances of the FID with various modes of operation of the IMS. Repetitive 0.1-μL injections of the gasoline sample were made under identical GC operating conditions. The split ratio was 50 to 1. Operating conditions are summarized in Table I.

Identification of Gasoline Components. Identifications of many of the components present in the gasoline sample were obtained by use of a Hewlett-Packard Model 5700 gas chromatograph interfaced with a Hewlett-Packard Model 5930 mass spectrometer and a Model 5934 data system. As the available GC/MS was equipped with a different type capillary column, standards were obtained for all components identified and retention times matched on the SE-54 column used in these studies. The order of compound elution agreed with that determined by Di Corcia et al., in studies on premium gasoline (*10*).

Reduced Mobility Studies. Ion mobility spectra were obtained for a number of compounds by continuously bleeding them into the instrument. The capillary column was removed from the ion mobility spectrometer and replaced with a short, noncoated fused silica transfer line terminating inside the oven of the gas chromatograph in a $^1/_4$ in. "tee" fitting. Glass sample holders containing individual compounds were attached to the branch of the "tee" while a constant nitrogen head pressure of 10 psi was provided to the remaining opening in the fitting and, therefore, to the transfer line. The amount of the compound entering the ion mobility spectrometer, determined by its vapor pressure, was controlled by varying the temperature of the GC oven.

RESULTS AND DISCUSSION

Salient Construction Modifications. While the ion separation region of this IMS design remains similar to that of earlier designs published in the literature, the ionization region is completely altered to make it more compatible with gas chromatography. Major changes in design are as follows:

First, the flow pattern of the drift gas has been altered to achieve a unidirectional flow in which the drift gas enters the instrument near the collecting electrode and travels in one direction through the drift and ionization regions to exit through a small orifice in the repeller plate. In earlier designs, gases entered at both ends of the tube to form an opposing flow scheme with an exit near the entrance gate to the ion separation region.

The second modification incorporates the use of a completely enclosed drift tube. Earlier IMS designs employed round insulator beads which created large openings between the guard rings. The instrument constructed for these studies utilizes insulator rings of borosilicate glass which interlock with the guard rings. Closing the drift tube in this manner permits undesired neutral species to be swept more efficiently from the separation and ionization regions. Increasing the surface area of the insulators in contact with the guard rings would be expected to create a small constant leakage current through the walls of the tube. For additional insulation for the collector electrode against this current, the last insulator ring was constructed of Teflon. Any leakage current present passes through a 1-MΩ resistor connected between the last guard ring and ground rather than across the Teflon insulator to the collector electrode. Leakage current is therefore prevented from contributing to detector background current or noise.

A third difference in design is a reduction in the cell volume of the ionization region. Typical cell volumes for ion mobility spectrometers or plasma chromatographs have been on the order of 7 cm^3 or larger. The cell volume in this instrument has been reduced to 1 cm^3, based on current designs for electron capture detectors. This reduction in size decreases the residence time of a compound in the ionization region to a few tenths of a second, maintaining the integrity of the gas chromatographic separation. It is interesting to speculate that if the center of ionization occurs within 2 mm of the ^{63}Ni foil as has been recently proposed by Aue and Kapila (*11*), it may be possible to reduce the cell volume more, decreasing further the resolution loss in the detector without affecting sensitivity.

The final change important for this detector is the introduction of the effluents from the GC column between the ionization region and the ion separation region. Thus the sample is swept away from the ion separation region and through the ionization region with the full velocity of the drift gas. In this configuration, neutral sample molecules, neutral products, or radicals are prohibited from interacting with product ions as they drift down the tube. Whether this configuration change causes subtle differences in product ions compared to those identified in the traditional configuration has not been established and will be the subject of a future investigation.

Reduced Mobility Constants. Several test compounds were continuously introduced into the IMS and ion mobility spectra obtained to determine the effect of modifications to this instrument on mobility data. Results of these studies are shown in Table II. For test compounds *n*-hexyl acetate and *n*-butyl acetate, one dominant product ion was observed in each ion mobility spectrum. This is in agreement with previous ion mobility spectra for these compounds (*12*). Reduced

Table II. Product Ion Reduced Mobilities

compound	K_0, cm² V⁻¹ s⁻¹ IMS	PLC
n-hexyl acetate	1.63	1.58
n-butyl acetate	2.00	2.00
1-octanol	1.46	1.45
	1.16	1.12
1-hexanol	1.81	1.76
	1.65	1.62
	1.18	1.18
1-butanol	1.78	1.77
	1.66	1.63

mobility constants were calculated from the following equation:

$$K_0\left(\frac{\text{cm}^2}{\text{V·s}}\right) = \frac{d}{tE} \times \frac{273}{T} \times \frac{P}{760}$$

where d = length of the ion separation region in centimeters, t = the drift time in seconds, and E = the electric field gradient in volts per centimeter. The latter two terms correct for experimental temperature and pressure conditions. The drift time for the product ion of *n*-hexyl acetate was 8.02 ms and that of *n*-butyl acetate was 6.55 ms. Reduced mobility constants calculated for these drift times were 1.63 cm²/V·s and 2.00 cm²/V·s, respectively. K_0 literature values are 1.58 cm²/V·s for *n*-hexyl acetate and 2.00 cm²/V·s for *n*-butyl acetate. Thus the K_0 value for the *n*-hexyl acetate product ion deviated only 3% from the literature value and the value for the *n*-butyl acetate product ion matched perfectly.

K_0 values from several alcohols known to produce multiple product ions were also compared to literature values. Results of these studies are also reported in Table II. All K_0 values calculated for these ions matched those of the literature within 4% and most were within 2% of the literature value (*13*). All measured mobilities either matched literature values or were slightly higher, indicating a consistent minor operating variation between this instrument and standard models. This may be attributed to any of the variety of parameters such as a different concentration of H_2O in the drift gas or a slight error in measuring electric field, temperature, pressure, or drift times. Whatever the reason the discrepancy appears to be minor. The general conclusion drawn from these studies is that the modified IMS exhibits ion mobility characteristics so similar to those of standard instruments that K_0 literature values of product ions can be used to predict approximate drift times in the modified IMS. In this newly constructed instrument, more precise calibration studies may eliminate these discrepancies altogether.

IMS as a GC Dectector. Knowing the drift times of specific reactant ions or product ions permits the IMS to continuously monitor drift time regions of interest and detect changes in ion current in those regions as a function of gas chromatographic elution time. Such chromatograms for a gasoline sample were obtained by using several drift time windows in the IMS and are compared to a standard FID tracing of the same sample. The standard FID chromatogram of the gasoline sample is shown in Figure 2. Some components in this sample have been identified with the aid of mass spectrometry and standards. Compounds in the gasoline sample which are important for this discussion are listed and assigned indentification numbers in Table III. Since the FID response is approximately proportional to the number of carbon atoms, a general decrease in responses in the latter portion of the chromatogram indicates a decrease in concentration levels for the high molecular weight compounds. This is, of course, exactly what one expects to see for a typical

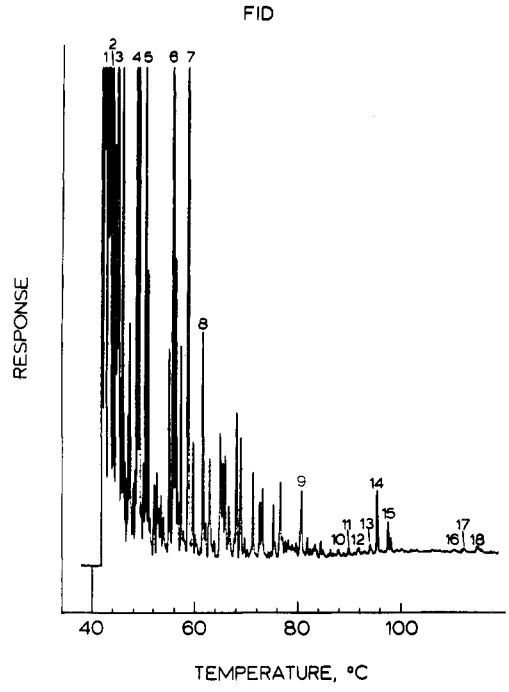

Figure 2. FID chromatogram of gasoline sample. The detector was operated under standard recommended conditions: H_2 = 30 mL/min, air = 350 mL/min, N_2 carrier = 0.5 mL/min, N_2(makeup) = 30 mL/min, detector temperature = 250 °C, electrometer attenuation = 4. Temperature program: initial = 40 °C, program = 2 °C/min, final = 100 °C, final hold = 10 min.

Table III. Peak Identifications

1	heptane
2	methylcyclohexane
3	toluene
4	*m*,p-xylene
5	*o*-xylene
6	trimethylbenzenes
7	ethyltoluene
8	*tert*-butylbenzene
9	naphthalene
10	dodecane
11	unknown
12	unknown
13	unknown
14	2-methylnaphthalene
16	1-methylnaphthalene
17	unknown
18	unknown

gasoline sample with flame ionization. Peak 10 corresponds to dodecane. With an external dodecane standard, the quantity of this compound introduced into the GC column (i.e., after allowing for the 50:1 split injection) was determined to be about 100 pg. As can be seen from Figure 2, this quantity is at the detection limit for the FID.

The chromatogram shown in Figure 3 was obtained, using the IMS, by selectively monitoring all ions having a drift time between 6 and 7 ms. Because this drift time window occurs before the reactant ion or product ion drift times, no response is seen even though a complicated mixture of gasoline components is eluting from the column and passing through the ionization region. This chromatogram illustrates a base line noise level for the detector of 0.02×10^{-12} A during a chromatographic run. This value represents a minimum noise level and does not include perturbations in the base line that may occur in an area where "chemical noise" such as fluctuations of ions produced from low levels of column bleed or the elution of ultratrace components in the sample is present.

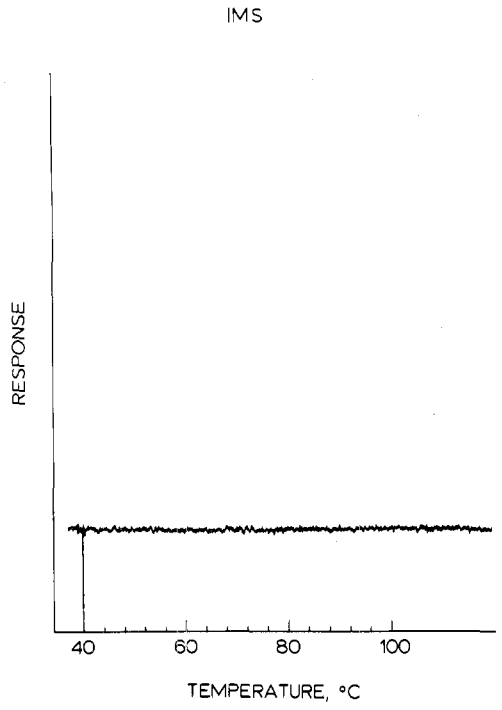

Figure 3. IMS noise level. Chromatogram of gasoline obtained by selectively monitoring ions having drift times between 6 and 7 ms. Entrance gate opened for 0.2 ms. Exit gate opened 6 ms later for 1 ms. Drift time window occurs before reactant and product ion drift times. Noise level = 0.02×10^{-12} A. Electrometer attenuation = 10.

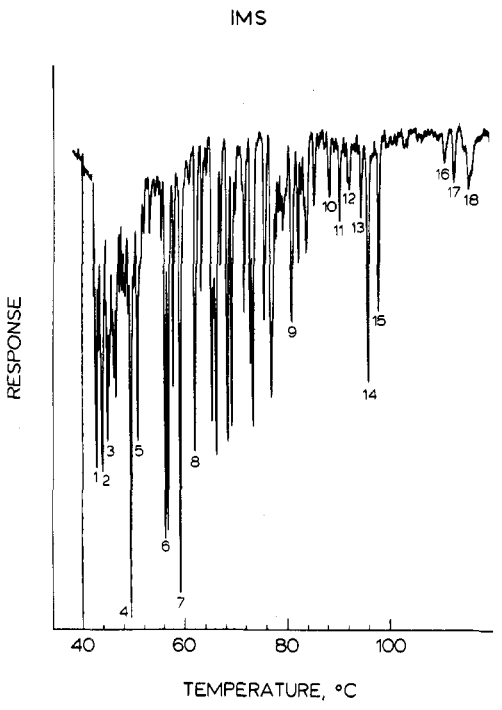

Figure 4. Nonselective reactant ion mode. Chromatogram of gasoline obtained by monitoring ions having drift times between 8 and 9 ms. Negative peaks represent a depletion of reactant ions by the chromatographic effluent.

Three positive reactant ions are observed in IMS when nitrogen or air is used as the drift gas. In order of decreasing mobility they are $(H_2O)_nNH_4^+$ and $(H_2O)_nNO^+$ where n = 0, 1, or 2 and $(H_2O)_nH^+$ where n = 2, 3, or 4. Although ionization pathways in ion mobility spectrometry are not well understood, some parallels have been drawn with ion molecule reactions occurring in chemical ionization mass spectrometry (CIMS). Searles and Sieck (*14*) have shown that normal, branched, or cyclic alkanes react with the NO^+ reactant ion to form $(M - 1)^+$ ions in a high-pressure photoionization mass spectrometer. This hydride transfer reaction becomes more exothermic as the number of carbon atoms increases. Further evidence on the reactivity of NO^+ with alkanes is provided by Karasek et al. (*15*). In ion mobility experiments they have shown that the intensity of the $(H_2O)_nNO^+$ reactant ion peak is greatly diminished when small quantities of alkanes are introduced into the instrument. In contrast, Griffin et al. (*16*) used an IMS coupled to a mass spectrometer to establish that both the $(H_2O)_nNO^+$ and $(H_2O)_nH^+$ reactant ions are responsible for production of the $(M + 1)^+$ ions which predominate when aromatic compounds are introduced into the ion mobility spectrometer. Such ions have also been shown to predominate in CIMS when methane is used as a reactant gas (*17*).

Operation of the IMS detector by continuously monitoring the drift time which coincides with that of the reactant ions results in a standing current corresponding to the continuous detection of these ions. When organic molecules enter the reaction region and undergo charge transfer reactions with these reactant ions to produce product ions with differing mobilities, the presence of the organic molecules is perceived as a decrease in standing current. For chromatographic elution of organic species this decrease in standing current takes the shape of a negative chromatographic peak with the standing current returning to its prior value as the organic is swept from the reaction region. Because the reactant ions being monitored charge transfer easily with most organic molecules to form heavier ions with slower mobilities, this mode of operation can be considered nonselective. Figure 4 illustrates a chromatogram of the gasoline sample which was obtained in this nonselective reactant ion mode. The sharp narrow peaks indicate that the individual components of the separation are being efficiently swept from the reaction region of the detector to retain the integrity of the chromatographic resolution. Some loss in resolution is noticeable when the IMS tracing is compared to the FID tracing, but this is not significantly different from that commonly observed between flame ionization and electron capture detectors. Also, the 3 ft transfer line is expected to contribute to band broadening. Nevertheless, these IMS chromatograms are orders of magnitude better, with respect to resolution, than any achieved with IMS in the past.

IMS chromatograms reported here were obtained as soon as the construction of the instrument was completed and without the aid of extensive optimization studies. Nevertheless, detection limits appear to be better than those of the FID with a minimum detectable quantity of 23 pg for dodecane in the IMS compared to the 100 pg value for the FID given earlier. Sensitivity can be increased by optimizing the electric field, drift length, and drift gas flow. However, sensitivity optimization based on changes in these parameters is complicated because they also affect the resolution characteristics of the ion mobility separation. Such studies will be the subject of further investigations. Because of continuous scanning operation, several ion mobility scans may be averaged to reduce noise and detection limits even further.

In contrast to the negative response mode the detector can be operated in a nonselective positive response mode by monitoring all product ions which drift with average velocities slower than those of the reactant ions. The tracing in Figure 5, obtained by detecting only those ions with drift times in excess of 10 ms, is essentially the inverse of that shown in Figure 4. Positive responses are seen for all components producing product ions with drift times between 10 and 20 ms, the normal product ion range. The two chromatograms match exactly with the exception of a few relatively large peaks which are observed in the chromatogram in the nonselective

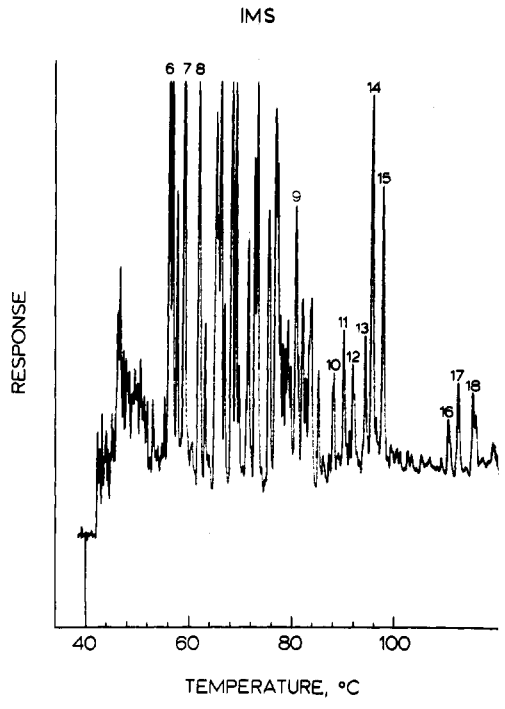

Figure 5. Nonselective product ion mode. Chromatogram of gasoline obtained by monitoring ions having drift times between 10 and 20 ms.

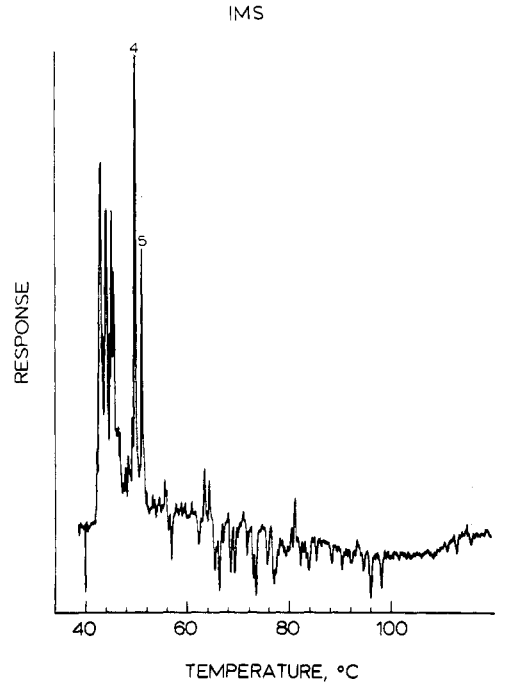

Figure 6. Selective product ion mode. Chromatogram of gasoline obtained by monitoring ions having drift times between 9 and 10 ms. Peak 4 (*m*- and *p*-xylene) and peak 5 (*o*-xylene) are selectively detected.

reactant ion mode but not in the nonselective product ion mode. This discrepancy can be explained as the formation of product ions with drift times in the 9–10 ms region. When the chromatogram was rerun while monitoring only the drift times between 9 and 10 ms, as shown in Figure 6, these peaks were observed as predominant peaks in the chromatogram. Peak 4 was identified via GC/MS and appropriate standards as including both *m*- and *p*-xylene. Peak 5 likewise was identified as *o*-xylene. Since this region still includes the tailing edge of the reactant ions, the chromatogram is complicated by the presence of small negative peaks due to

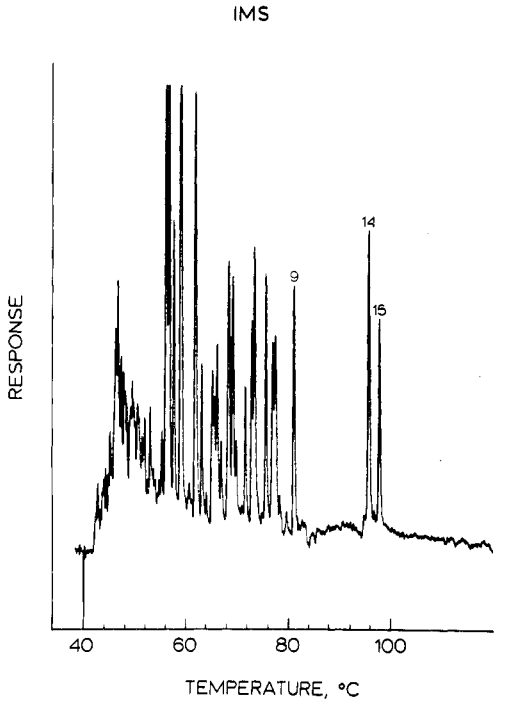

Figure 7. Selective product ion mode. Chromatogram of gasoline obtained by monitoring ions having drift times between 10 and 11 ms. Peaks 9 (naphthalene), 14 (2-methylnaphthalene), and 15 (1-methylnaphthalene) are selectively detected. Compare with Figure 5.

reactant ion depletion by other components in the sample.

Such selective monitoring of product ions is perhaps the principal advantage of ion mobility detection in gas chromatography for it permits the investigator the luxury of tuning the detector to monitor compounds that may be of specific interest. Figure 7 is an example of selective product ion monitoring where only the product ions with drift times between 10 and 11 ms are detected. On comparison of this figure with Figure 5, the advantages become immediately obvious. Many peaks observed in the nonselective mode were predictably not present or were descriminated against in the selective mode. Spectacular selectivity was achieved for peaks 9, 14, and 15 since all other peaks in this area of the chromatogram were undetected. These three compounds, in order of elution, have been identified as naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene. Differing only in the addition and/or position of a methyl group, these compounds would be expected to form product ions with similar drift times. Their detection illustrates the potential of the ion mobility spectrometer for sensitive and selective determination of trace quantities of organic compounds in complex samples.

In the past, ion mobility spectrometry has often been inappropriately described as low-resolution mass spectrometry which can be performed at atmospheric pressure. Spectra, however, are a function of ion mobilities rather than mass to charge ratios and often do not provide sufficient information for absolute identification. Considering the current understanding of atmospheric pressure ion fragmentation, clustering chemistry, and ion mobilities it is more appropriate to view and apply IMS as a tunable selective detector for gas chromatography rather than as an identification technique in competition with mass spectrometry. Investigations of advantages and disadvantages of this technique as compared to those of electron capture, flame ionization, photoionization, flame photometric, and other GC detectors will serve best to determine the analytical usefulness of ion mobility spectrometry. The instrument described in this paper is particularly well suited for such investigations. From the preliminary results presented here, ion mobility spectrometry as a

GC detection method may have a broad range of unique applications in the field of trace organic analysis.

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Potentiometric Detection System for Flow Injection Titrimetry

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A new potentiometric detection system for use in flow injection titrimetry was designed and investigated. An antilogrithmic amplifier provides a signal related to proton concentration and enables manual selection of system sensitivity. A description of the microelectrodes used as potentiometric sensors is provided. Precision within a set of titrations averaged 0.8% RSD and unknowns were determined with an average error of 4%.

Since its introduction in 1975 (*1*), flow injection analysis (FIA) has generated considerable interest among researchers (*2–6*). The flexibility of the technique is exemplified by its use in enzymatic determinations (*7*), extraction (*8*), and dialysis (*9*). Since FIA requires only a small sample (20–200 μL), it is a potentially useful tool for routine analysis in clinical laboratories. Rapid sampling and analysis rates inherent in FIA coupled with a variety of methods of detection further increase the range and adaptability of the technique.

A number of authors have studied titrations in detail using FIA methodology (*3, 10–12*). One important difference between flow injection titrimetry (FIT) and other FIA procedures is the use of peak width rather than peak height for the quantitation of analytical data. As shown by Ruzicka and co-workers (*11*), peak width measured in units of time is linearly related to the logarithm of the concentration of analyte. In order to use peak width as the experimental measurable, a large dispersion effect at the sample–carrier stream interface is advantageous because it serves to increase precision. In FIA, dispersion is usually created by placing a mixer between the sample injector and the detector. However, a recent publication suggests that FIA titrations may be performed without the use of a gradient mixer (*12*). In addition, the high accuracy and precision of electronic timers greatly facilitates the precise measurement of peak widths. As a result, the precision of the data is limited by other factors such as the sensitivity of the detector and the precision of the flow rate.

When applicable, potentiometric detectors have been used in FIA with favorable results (*3, 6, 7, 11, 13–16*), and the performance of ion-selective electrodes has been evaluated in previous reports (*13, 17*). Although potentiometric detectors offer advantages which complement the FIA method (simplicity, high specificity, and ruggedness), they are not without limitations. One limitation is the instability of base line voltage levels. Pulsing of the stream resulting from the peristaltic pumps often used in FIA systems tends to generate static charges within the stream. These charges affect the stability of the reference and indicator electrode signals. Consequently, a stable base line voltage may be achieved only with difficulty, which lowers sensitivity and raises detection limits.

In this report, we present a simple, inexpensive electronic detection system for use with potentiometric sensors in flowing streams. The instrument may be easily adjusted to compensate for small drifts, and it has provision for manual selection of sensitivity. This allows the operator to choose a detection limit which is consistent with a given set of experimental conditions.

The operation of the instrument was evaluated by titrating NaOH with HCl. Samples of the base were introduced into a stream of HCl using a rotary injection valve (*18*). Long-term and short-term studies of precision were conducted to determine day to day reproducibility. Titrations of pseudounknowns served as checks on the accuracy of the instrument. The results of these studies are detailed below.

EXPERIMENTAL SECTION

Apparatus. A block diagram of the experimental arrangement is displayed in Figure 1. The sample injection block was a

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