# Ion Mobility Detector for Gas Chromatography with a Direct Photoionization Source

Michael A. Baim, Randy L. Eatherton, and Herbert H. Hill, Jr.*

*Department of Chemistry, Washington State University, Pullman, Washington 99164-4630*

**An ion mobility detector (IMD) for gas chromatography has been modified to accept the use of a photoionization source. Photoionization offers a number of advantages over the commonly employed $^{63}$Ni foil including the lack of reactant ions, which are seen with the secondary ionization source, enabling use of the entire ion mobility spectrum from 0 to 20 ms for observation of product ions. Test compounds continuously bled into the detector are used to compare performance of the standard $^{63}$Ni foil to that of a low-pressure 10.0-eV krypton photoionization lamp. Due to uncomplicated fragmentation patterns produced via photoionization, the tunable selective capabilities of the detector are enhanced. Selective mobility monitoring is used to detect toluene, mesitylene, and naphthalene in a mixture of aromatic compounds of similar structure following separation on a fused silica capillary column.**

Ion mobility spectrometry (IMS) has long been recognized as a potentially useful technique for selective detection of organic compounds after separation by gas chromatography (1-7). First introduced in 1970 by Cohen and Karasek (8, 9), the ion mobility spectrometer consists of two basic units: a $^{63}$Ni foil in an ionization cell analogous to that found in an electron capture detector (ECD) and an atmospheric pressure ion drift tube maintained at either a positive or negative uniform electric field gradient of 150-250 V/cm. Ions produced in the ionization cell are accelerated down the electric field where they are separated according to their mobilities in a countercurrent flow of nitrogen gas. As discussed by Revercomb and Mason (10), a number of factors including the mass, size, and charge of an ion determine its mobility at atmospheric pressure.

The prime advantage of IMS as a GC detection method is that the instrument may be easily tuned to monitor ions of a preselected mobility, thereby tailoring response characteristics to fit the needs of a given separation problem. Ion mobility spectrometry can often provide selective detection between compounds of the same elemental content but differing in structural composition. Despite these advantages, however, IMS has not enjoyed wide-scale popularity as a GC detection technique largely due to limited success at interfacing the instrument with chromatographic columns.

A new GC detector based on the principles of IMS has been developed in this laboratory specifically to eliminate many of the limitations preventing use with high-resolution separations (11). Known as the ion mobility detector (IMD), this instrument has been used to selectively detect a wide range of compounds including substituted naphthalenes in gasoline (11) and terpenes in orange extract (12) using the positive ion mode and 2,4-dichlorophenoxyacetic acid in soil extracts (13) using the negative ion mode. Investigations into the response characteristics of the IMD have shown it to be extremely sensitive to organic compounds. Minimum detectable amounts are typically in the low picogram range and detector response is exponential with weight injected over approximately 2 orders of magnitude (usually 1-100 pg) (14).

The $^{63}$Ni foil is a secondary ionization source which ionizes compounds by a series of charge transfer reactions (15-17). Response is nonlinear, and as with other charge transfer ionization sources such as corona discharges and chemical ionization, reactant ions can undergo interfering reactions with contaminating compounds including column bleed and unresolved components in the sample mixture. As reactant ions are depleted by these competing reactions, response to the compound of interest can become erratic or, in extreme cases, be eliminated entirely. Replacement of the $^{63}$Ni foil with an atmospheric pressure primary ionization source would be expected to yield a significant reduction in interferences thereby enhancing the ability of the detector to reliably handle complex samples.

Recent investigations by Lubman and Kronick have demonstrated that ultraviolet light from a Nd:YAG pumped pulsed laser system can be used at atmospheric pressure to produce ions in an ion mobility spectrometer (18-20). For a more general ionization source capable of ionizing most organic compounds, an ArF excimer laser (194 nm) has also been examined (20).

Photoionization accomplished through the use of a short wavelength UV lamp, such as those routinely used in photoionization detectors for gas chromatography, would be expected to be an inexpensive, practical alternative to laser sources for use in an ion mobility GC detector. Detectors using direct, single photon ionization of organic compounds by ultraviolet light have been known to chromatographers for a number of years. Innovations in sealing the low-pressure UV light source and separating it from the detector ionization cell have enabled the use of photoionization as a method for producing ions at atmospheric pressure (21-24). In recent years the atmospheric pressure photoionization detector (PID) has become a sensitive and reliable instrument for the detection of aromatic and other unsaturated organic compounds (25-28) with several investigators examining its proposed response mechanisms and operating characteristics (29-32). An ion mobility detector equipped with a UV photoionization source would have the additional ability to selectively monitor compounds which respond universally in the standard PID. The objective of this work was to examine the feasibility of using a UV lamp as an ionization source for the ion mobility detector previously constructed. Both continuous bleed ion mobility spectra and gas chromatograms obtained by using the photoionization equipped ion mobility detector will be presented.

## EXPERIMENTAL SECTION

**Design of the Ionization Cell.** Design and construction of the ion mobility detector with a $^{63}$Ni ionization source have been previously reported (11). Since the publication of this design, two minor modifications have been made to the drift tube. First, the distance between the entrance and exit gates has been increased from 4.8 cm to 7.5 cm by the addition of three stainless steel guard rings. Used in a portion of earlier studies, the longer drift length increases the ability of the detector to separate ions of similar mobilities. Second, the passive gate installed between the exit gate and the collector electrode has been removed. Although it has often been claimed that the passive gate serves
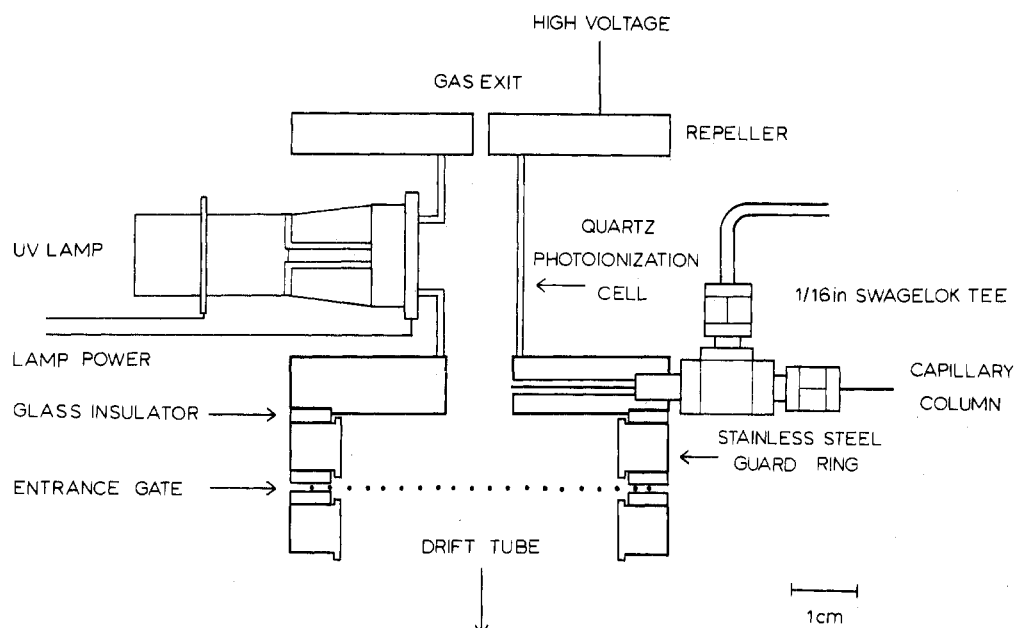
**Figure 1.** Schematic diagram of ion mobility detector ionization cell with photoionization source installed.

to insulate the collector from transient noise generated by pulsing of the exit gate, no deleterious effects on detector performance were noted after its removal.

A schematic diagram of the detector ionization cell with the UV lamp installed is provided in Figure 1. In order to facilitate comparisons between the two ion sources, the photoionization cell was designed as a direct replacement for the ionization cell containing the $^{63}$Ni foil. A new guard ring with an internal diameter of 1.0 cm was machined and drilled radially to accept the sample inlet. The ionization cell itself is a quartz tube, 1.1 cm i.d. × 3.0 cm long, with a 10.0-eV (123.6 nm) krypton lamp (Tracor Instruments, Austin, TX) mounted perpendicular to the direction of gas flow through the cell. Because quartz is not transparent to radiation of this wavelength, the ionization cell was flared slightly, drilled out, and sealed with an O-ring to the magnesium fluoride window of the UV lamp. Lamp current was supplied by a Tracor Model 703 current-limiting photoionization power supply.

Regardless of which ion source is in use, the mechanics of detector operation remain the same. Organic compounds entering the detector via the sample inlet are swept through the ionization cell by typically 600–800 mL/min of prepurified nitrogen used as the drift gas. When a positive electric field is applied to the repeller and drift tube, as was used in these studies, positive ions are accelerated down the field for separation according to mobilities. Ions are gated into the separation region of the drift tube by briefly removing a strong electric field applied to the entrance gate. Depending on the time delay between pulsing of the entrance and exit gates, only ions of the corresponding mobility are able to migrate down the tube to the collector without being neutralized on the gate wires. Through the use of an AIM 65 microcomputer (Rockwell International, Anaheim, CA) the delay between pulsing of the entrance and exit gates may be progressively increased to provide an ion mobility spectrum of an organic compound continuously bled into the detector or it may be set at a fixed interval to monitor ions of a preselected mobility as a complex mixture of compounds sequentially elutes from a chromatographic column.

Operating parameters of the IMD common to all experiments performed were as follows: ion drift length, 7.5 cm; electric field gradient, +230 V/cm; temperature, 150 °C; photoionization lamp current (when used as the ion source), 2.5 mA. Drift and make-up gases were both prepurified nitrogen (Liquid Air, Inc., San Francisco, CA). Gas flow rates for the $^{63}$Ni equipped detector were drift gas 600 mL/min and make-up gas 20 mL/min while those for the photoionization equipped detector were drift gas 800 mL/min and make-up gas 250 mL/min. Analytical standards (Chem Service, Inc., West Chester, PA) were used "neat" for the continuous bleed ion mobility studies or prepared as mixtures in hexane (J. T. Baker Chemical Co., Phillipsburg, NJ) for analysis by gas chromatography.

**Ion Mobility Studies.** In order to directly compare performance of the two ion sources, ion mobility spectra were obtained for background or reactant ions and several organic compounds using both the $^{63}$Ni foil and the UV lamp. Glass sample holders containing individual compounds were attached to the branch of a $^1/_4$ in. "tee" fitting inside the oven of a gas chromatograph. Nitrogen gas, supplied via an unused injection port, was passed through the tee fitting and into a short length of noncoated fused silica transfer line (Hewlett-Packard Co., Avondale, PA) used to connect the sampling apparatus to the ion mobility detector. The amount of compound entering the IMD, varied as necessary to produce spectra of approximately the same signal intensity, was controlled by varying the nitrogen head pressure and temperature of the GC oven. Concentrations on the order of 1–5 ppm were used for all compounds studied. To obtain an ion mobility spectrum, the entrance gate was pulsed open for 0.2 ms once every 20 ms. The exit gate was also pulsed open for 0.2 ms following a time delay that slowly increased from 0 to 20 ms thus scanning the entire reactant and product ion range.

**Gas Chromatography.** Gas chromatograms illustrating use of the photoionization equipped IMD as a tunable selective detector were obtained with a Tracor Model 560 capillary chromatograph (Tracor Instruments, Austin, TX) operated in the split injection mode. Separation of a ten-compound aromatic test mixture was performed on a 30-m DB5 bonded phase fused silica capillary column (J and W Scientific, Inc., Rancho Cordova, CA) with a carrier gas flow rate (helium) of 1.5 mL/min. The injection port temperature was maintained at 250 °C and the GC oven was temperature programmed from 35 °C to 150 °C at 10 °C/min. Chromatograms, produced by repetitive injections, correspond to 150 ng of each mixture component after allowing for the 50:1 split injection employed. The capillary column was routed 3 ft to the detector oven through an insulated transfer line maintained at 150 °C.
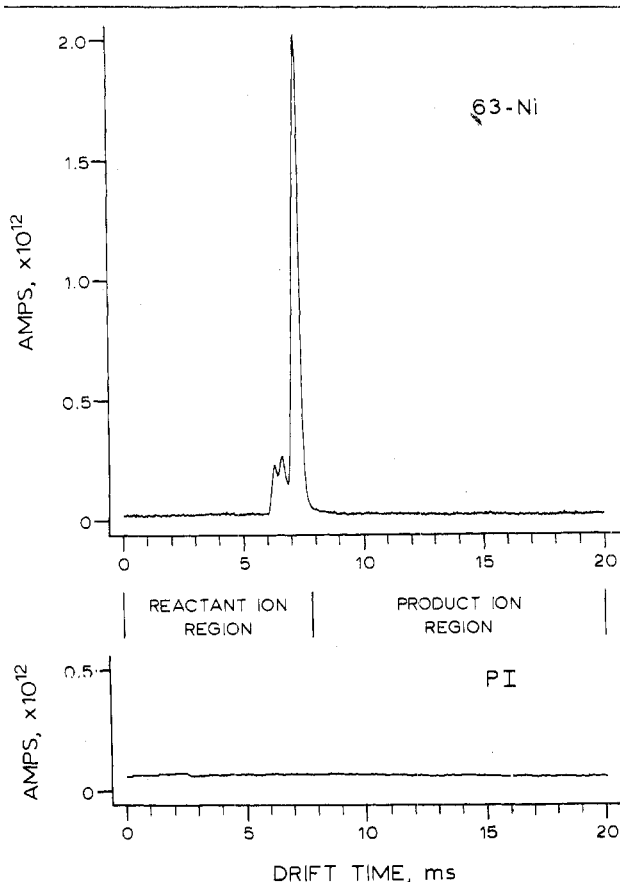
## RESULTS AND DISCUSSION

**Comparison of Ionization Sources.** Results obtained from ion mobility scans of background or reactant ions and three aromatic compounds continuously bled into the detector using both $^{63}$Ni and photoionization sources are presented in Table I. Data are reported in terms of the reduced mobility, $K_0$, which may be calculated from the drift time of the peaks (11).

Figure 2 illustrates background ion mobility spectra obtained with no organic species present in the detector. With the $^{63}$Ni ionization source, three positive reactant ion cluster peaks are observed in agreement with previous ion mobility studies. Species forming these three reactant ion peaks have
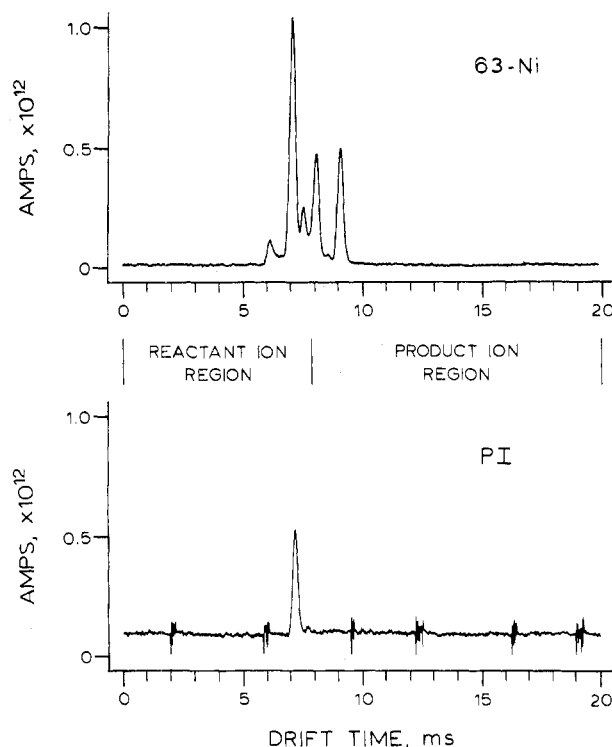
Table I. Reactant and Product Ion Reduced Mobilities

| compound | $K_0$, cm$^2$ V$^{-1}$ s$^{-1}$ | |
| --- | --- | --- |
| | $^{63}$Ni | PI |
| reactant ions | 2.97 | |
| | 2.84 | |
| | 2.60 | |
| benzene | | 2.61 |
| | 2.48 | 2.45 |
| | 2.33 | |
| | 2.08 | |
| naphthalene | 2.14 | 2.21 |
| | 2.03 | 2.09 |
| | 1.87 | 1.90 |
| tert-butylbenzene | | 2.34 |
| | 2.21 | 2.18 |
| | 2.03 | 2.01 |
| | 1.75 | 1.74 |



Figure 2. Comparison of ion mobility spectra using $^{63}$Ni and photoionization (PI) sources with no organic sample present in the detector.



Figure 3. Comparison of benzene ion mobility spectra using $^{63}$Ni and photoionization (PI) sources.

been identified by combined ion mobility spectrometry/mass spectrometry as, in order of decreasing mobilities, $(H_2O)_n NH_4^+$, $(H_2O)_n NO^+$, and $(H_2O)_n H^+$ where the value of $n$ is dependent on temperature and water concentration in the system (33). Notice the stability of the base line and lack of product ion peaks indicating that the IMD is free from contamination. When the $^{63}$Ni source is replaced by the UV lamp, and the same scan is repeated, a flat base line extending the full width of the ion mobility spectrum from 0 to 20 ms is produced. Only prepurified nitrogen flows through the detector ionization cell when no organic compounds are present. Because the ionization potential of nitrogen (15.58 eV) is considerably above the energy of the 10.0-eV Kr lamp, no ionization occurs and hence no peaks are observed.

A significant advantage to the use of a photoionization source is immediately apparent when the two ion mobility spectra in Figure 2 are compared. Reactant ions present in the $^{63}$Ni ionization spectrum obscure a portion of the ion

mobility scan, from 6 to 8 ms. Any organic compounds producing product ions of similar mass and size would be expected to have mobilities similar to those of the reactant ions and thus also appear in this region. Such product ions would be impossible to observe as discrete peaks separate from the reactant ions. Therefore, selective product ion mobility monitoring in this region, for purposes of compound detection following gas chromatography, could not be accomplished. In contrast, the photoionization spectrum is totally unobscured. Product ions with mobilities occurring anywhere in the 0 to 20 ms range may be selectively monitored without interference from reactant ion responses.

One example of overlapping reactant and product ion peaks is presented in Figure 3. Ion mobility spectra were obtained for benzene, using each ionization source, by continuously bleeding a small amount of the compound into the detector. Three product ion peaks are present in the $^{63}$Ni spectrum, the first two of which are not completely resolved from the $(H_2O)_n H^+$ reactant ion peak. Kim et al. used a combined ion mobility spectrometer/mass spectrometer to identify three product ions resulting from ion–molecule reactions between benzene and the reactant ions normally present in the instrument (34). These ions, identified as M$^+$, MH$^+$, and MNO$^+$ where M represents neutral benzene, appeared to change mobility as a function of temperature due to changes in the amount of clustering with neutral water and nitrogen molecules. At temperatures below 150 °C, the M$^+$, MH$^+$, and $(H_2O)_n H^+$ peaks were almost totally overlapping leaving the MNO$^+$ peak, which was much lower in relative intensity, as the only benzene product ion suitable for selective mobility monitoring. Even at temperatures above 200 °C, where ion–molecule clusters with $H_2O$ and $N_2$ were no longer observed, significant overlap between the M$^+$, MH$^+$, and $(H_2O)_n H^+$ peaks still persisted. Although $K_0$ values for benzene product ions observed in these experiments differ slightly from those calculated by Kim and co-workers, the same type of peak overlap is seen.

Replacing the $^{63}$Ni ionization source with the UV lamp and again scanning the benzene ion mobility spectrum yields

distinctly different results. A single, large product ion peak with a drift time of 7.31 ms ($K_0 = 2.61$ cm$^2$ V$^{-1}$ s$^{-1}$) is observed along with a very small peak at 7.80 ms ($K_0 = 2.45$ cm$^2$ V$^{-1}$ s$^{-1}$). The drift time corresponding to the major product ion peak is virtually identical with that of the $(H_2O)_nH^+$ reactant ion ($t = 7.37$ ms) seen with $^{63}$Ni ionization; yet, because no reactant ions exist under photoionization conditions, the product ion peak is not obscured. Monitoring this drift time while a complex organic mixture elutes from a GC column would allow detection of benzene without competition from changing concentrations of reactant ions.

A small amount of ion leakage current passing through the two gates is indirectly responsible for the small, sporadic fluctuations seen in the base line of the benzene ion mobility scan obtained by using the photoionization source. The GC oven was operated at ambient temperature for benzene causing the sample reservoir end of the fused silica transfer line to also remain cool. It is believed that small "plugs" of the liquid sample were condensing in the end of the transfer line briefly interrupting sample flow into the detector. With the photoionization source, ions are produced only when an organic sample is present in the detector ionization cell. Therefore, momentary flow interruptions as the transfer line plugged and cleared itself could have resulted in the sharp base line fluctuations observed. Such fluctuations were not observed when the $^{63}$Ni secondary ionization source was installed because the total number of ions present in the detector, and hence the ion leakage current, remains essentially constant regardless of interruptions in sample flow. Since in virtually all routine work the IMD is operated as a GC detector and is therefore connected to a fused silica capillary column, no attempt has been made to redesign the sampling apparatus. No base line fluctuations have been observed in GC studies.

Ion mobility spectra of two additional compounds are presented in Figure 4. As evident in Table I, product ion mobilities are quite similar for a given compound regardless of which ion source was employed. Naphthalene (Figure 4A) exhibits two major product ions and a small shoulder when the $^{63}$Ni source is used. Switching to photoionization causes a dramatic change in relative intensity with the product ion of highest mobility ($K_0 = 2.21$ cm$^2$ V$^{-1}$ s$^{-1}$) becoming significantly more intense than the other peaks. Unfortunately, no ion mobility product ion identifications are available in the literature for naphthalene and suitable mass spectrometry facilities to perform such experiments do not exist in this laboratory. Nevertheless, loss of an electron to form the molecular ion $M^+$ is considered to be the predominant ionization pathway in photoionization detectors (23, 29) and the major product ion peak appearing in the photoionization ion mobility spectrum ($K_0 = 2.21$ cm$^2$ V$^{-1}$ s$^{-1}$) may be tentatively attributed to the naphthalene molecular ion. tert-Butylbenzene (Figure 4B) exhibits essentially the same product ion peaks, in both drift time and relative intensity, when either ionization source is employed. The one exception is a small product ion peak at approximately 8.2 ms which appears distinctly only under photoionization conditions. The tailing edge of the reactant ion peak appears to partially obscure this product ion peak when the $^{63}$Ni ionization source is used. No product ion identities for tert-butylbenzene are available in the literature.

**Photoionization IMD for Capillary GC.** A series of four fundamental modifications to previously available instrument designs has enabled efficient interfacing of the ion mobility detector to chromatographic columns. These modifications, reported previously in the literature (11, 12), will not be discussed again here. The tunable selective detection capabilities of the IMD rely on differences in mobilities of product ions produced from the components of a sample mixture. An
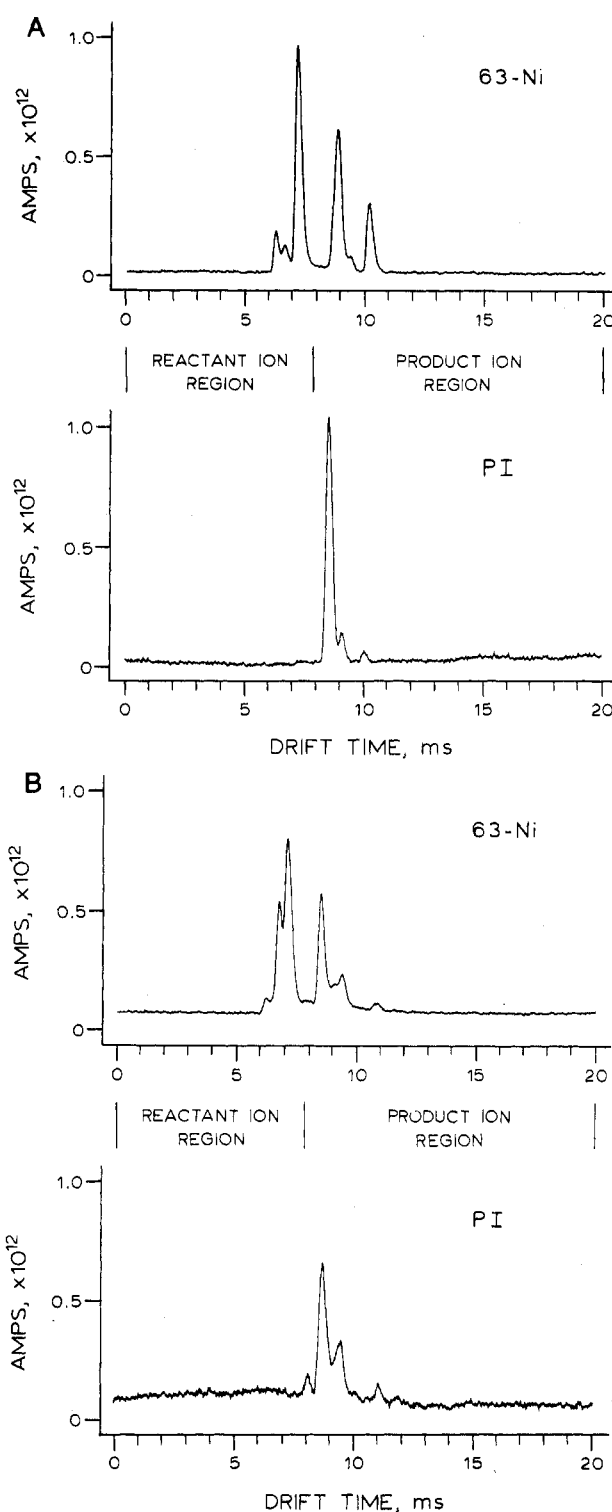


**Figure 4.** (A) Comparison of naphthalene ion mobility spectra using $^{63}$Ni and photoionization (PI) sources. (B) Comparison of tert-butylbenzene ion mobility spectra using $^{63}$Ni and photoionization (PI) sources.

ionization source, such as the UV lamp used in these studies, which produces uncomplicated ion mobility spectra reduces the potential for interferences among multiple product ions of compounds not fully separated by the GC column. A test mixture containing ten aromatic compounds was prepared to evaluate performance of the photoionization equipped ion mobility detector. A list of the test compounds, in order of elution, is given in Table II.

The IMD may be tuned to monitor all product ions produced in the detector ionization cell in which case a nonse-
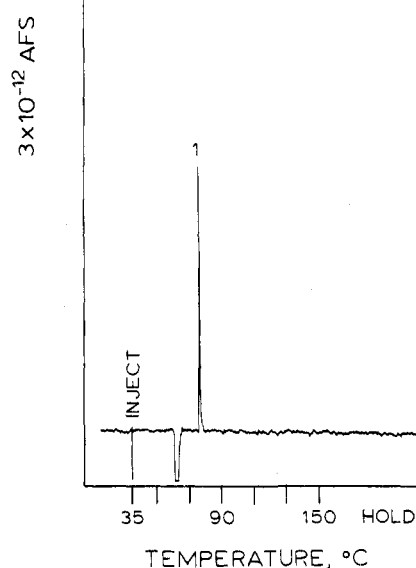
Table II. Compounds in GC Test Mixture

| 1 | toluene |
|---|---|
| 2 | ethylbenzene |
| 3 | o-xylene (1,2-dimethylbenzene) |
| 4 | cumene (isopropylbenzene) |
| 5 | mesitylene (1,3,5-trimethylbenzene) |
| 6 | tert-butylbenzene |
| 7 | p-cymene (1-isopropyl-4-methylbenzene) |
| 8 | durene (1,2,4,5-tetramethylbenzene) |
| 9 | naphthalene |
| 10 | phenylcyclohexane |
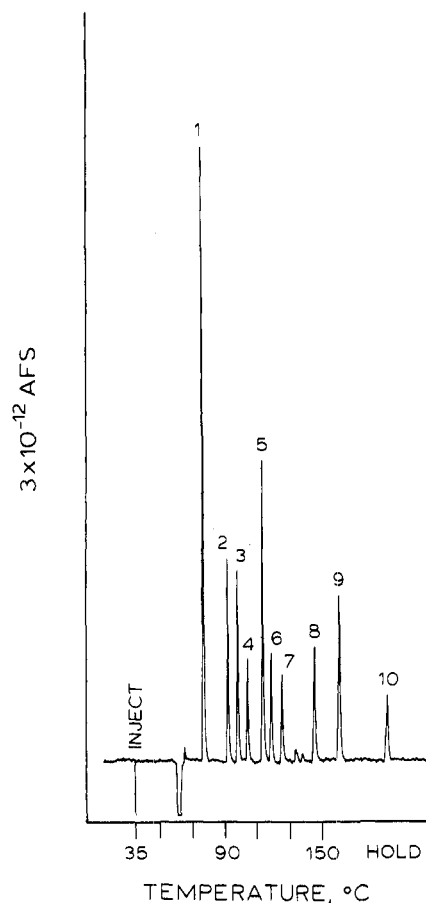


Figure 5. Nonselective product ion chromatogram obtained by monitoring ions with drift times between 7.0 and 15.0 ms. Compound identities are given in Table II.



Figure 6. Selective product ion chromatogram obtained by monitoring ions with drift times between 7.0 and 7.5 ms. Toluene is selectively detected.

lective response toward organic compounds, analogous to that of a flame ionization detector (FID), is generated. When the IMD is equipped with the photoionization source, response is enhanced for aromatic and other unsaturated compounds relative to response of saturated compounds like alkanes as has been shown in comparisons between conventional photoionization and flame ionization detectors (25–28). Figure 5 illustrates a chromatogram obtained in this nonselective mode by monitoring all product ions with drift times between 7.0 and 15.0 ms. (No product ions with drift times in excess of 15 ms were observed for this sample.) Positive responses are seen for all ten test compounds. Relative peak intensities match those obtained by use of a standard Tracor Model 703 photoionization detector in place of the IMD. Because its ionization cell volume is much smaller than that of the IMD, the Tracor PID produced somewhat less peak broadening. The negative response prior to the toluene peak corresponds in retention time to the dead volume of the column. It is most likely due to quenching of a small detector background current by air introduced with the sample. This nonselective mode of operation is useful for detection of uncomplicated samples

and, in the case of compounds producing more than one product ion, can be more sensitive than selective modes since all product ions contribute to response.

Dramatic selectivity, even among compounds of similar structure, can often be achieved by monitoring a narrow drift time range. In Figure 6, a chromatogram produced by monitoring those product ions with drift times between 7.0 and 7.5 ms is shown. Although the sample injected was the same as that used to produce the chromatogram in Figure 5, only one peak, corresponding to toluene, is seen. All other compounds, having no product ions with drift times in this range, are undetected. It is interesting to note that it may not be possible to obtain this selective chromatogram by using the IMD equipped with a $^{63}$Ni source. Assuming that a toluene product ion of similar mobility is produced under $^{63}$Ni ionization conditions, a comparison with the reactant ion scan in Figure 2 shows that it would not be resolved from the $(H_2O)_nH^+$ reactant ion peak. Selective detection of toluene would only be possible if another product ion, well separated from the $^{63}$Ni reactant ions and the product ions due to other compounds, could be located.

A final example of selective mobility monitoring is presented in Figure 7. The IMD was tuned to monitor only those product ions with drift times between 8.2 and 8.7 ms. Peaks 5 and 9, corresponding to mesitylene and naphthalene, respectively, are selectively detected. Compounds 1, 2, 4, and 6 produced small responses indicating that some overlap among product ion spectra is still present. The four remaining compounds in the mixture were not detected.

The ion mobility detector used in these experiments was retrofitted with the photoionization cell in order to ease comparisons between the two ion sources and, as such, the cell does not necessarily represent the ideal design. Comparing
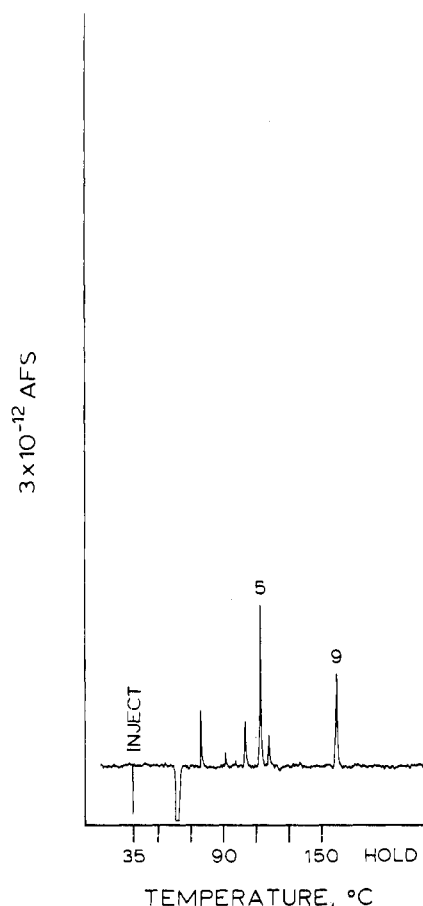
**Figure 7.** Selective product ion chromatogram obtained by monitoring ions with drift times between 8.2 and 8.7 ms. Mesitylene (5) and naphthalene (9) are selectively detected.

the chromatographic resolution of the photoionization equipped IMD in Figures 5–7 with that obtained with the $^{63}$Ni ionization cell (see, for example, ref 11) shows a noticeable loss of resolution upon changing to the photoionization source. This is not surprising, however, when the volumes of the two ionization cells are compared. While the $^{63}$Ni cell displaces a volume of 1 cm$^3$, the photoionization cell is approximately three times as large due to lamp mounting limitations and other detector dimensions. In addition, the photoionization detector is concentration dependent (29) so sensitivity is reduced by the large cell volume. In these studies sensitivity was further reduced by the high drift and make-up gas flows required to keep resolution at an acceptable level. Knowledge gained from these experiments has been applied to the design of a new photoionization IMD which should have resolution and sensitivity characteristics more equivalent to those of commercially available photoionization detectors for gas chromatography.

From the results of the continuous bleed ion mobility studies and the capillary gas chromatograms shown it may be concluded that direct photoionization of organic compounds with a low-pressure UV lamp is a viable technique for use with the IMD. In all cases, product ion spectra obtained were no more complex than those obtained with the $^{63}$Ni source. In fact, significantly simpler spectra were obtained for benzene and naphthalene. When applied as a GC detector, the photoionization IMD has an unrestricted product ion range making it suitable for selectively detecting low molecular weight compounds whose product ions are normally obscured by reactant ions under $^{63}$Ni ionization conditions. Low-pressure UV lamps with a wide range of energies are now available from a number of manufacturers at costs competitive with that of a 15-mCi $^{63}$Ni foil. Either more selective or more universal ionization of organic compounds may thus be obtained depending on analysis requirements.

## LITERATURE CITED

(1) Karasek, F. W.; Keller, R. A. *J. Chromatogr. Sci.* **1972**, *10*, 626–628.
(2) Karasek, F. W.; Kim, S. H. *J. Chromatogr.* **1974**, *99*, 257–266.
(3) Karasek, F. W.; Hill, H. H., Jr.; Kim, S. H.; Rokushika, S. *J. Chromatogr.* **1977**, *135*, 329–339.
(4) Cram, S. P.; Chesler, S. N. *J. Chromatogr. Sci.* **1973**, *11*, 391–401.
(5) Boggs, G. U.; Tou, J. C. *Anal. Chem.* **1976**, *48*, 1351–1357.
(6) Ramstad, T.; Nestrick, T. J.; Tou, J. C. *J. Chromatogr. Sci.* **1978**, *16*, 240–245.
(7) Ithakissios, D. S. *J. Chromatogr. Sci.* **1980**, *18*, 88–92.
(8) Cohen, M. J.; Karasek, F. W. *J. Chromatogr. Sci.* **1970**, *8*, 330–337.
(9) Cohen, M. J. U.S. Patent No. 3 626 178, Dec 7, 1972.
(10) Revercomb, H. E.; Mason, E. A. *Anal. Chem.* **1975**, *47*, 970–983.
(11) Balm, M. A.; Hill, H. H., Jr. *Anal. Chem.* **1982**, *54*, 38–43.
(12) Balm, M. A.; Schuetze, F. J.; Frame, J. M.; Hill, H. H., Jr. *Am. Lab.* (*Fairfield, Conn.*) **1982**, *14*, 59–70.
(13) Balm, M. A.; Hill, H. H., Jr. *J. Chromatogr.*, in press.
(14) Balm, M. A.; Hill, H. H., Jr. *HRC CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* **1983**, *6*, 4–10.
(15) Karasek, F. W.; Denny, D. W.; DeDecker, E. H. *Anal. Chem.* **1974**, *46*, 970–973.
(16) Griffin, G. W.; Dzidic, I.; Carroll, D. I.; Stillwell, R. N.; Horning, E. C. *Anal. Chem.* **1973**, *45*, 1204–1209.
(17) Karasek, F. W.; Denny, D. W. *Anal. Chem.* **1974**, *46*, 633–637.
(18) Lubman, D. M.; Kronick, M. N. *Anal. Chem.* **1982**, *54*, 1546–1551.
(19) Lubman, D. M.; Kronick, M. N. *Anal. Chem.* **1982**, *54*, 2289–2291.
(20) Lubman, D. M.; Kronick, M. N. *Anal. Chem.* **1983**, *55*, 867–873.
(21) Sevcik, J.; Krysl, S. *Chromatographia* **1973**, *6*, 375–380.
(22) Ostojik, N.; Sternberg, Z. *Chromatographia* **1974**, *7*, 3–5.
(23) Driscoll, J. N.; Spaziani, F. F. *Res./Dev.* **1976**, *27*, 50–54.
(24) Driscoll, J. N. *J. Chromatogr.* **1977**, *134*, 49–55.
(25) Driscoll, J. N.; Ford, J.; Jaramillo, L. F.; Gruber, E. T. *J. Chromatogr.* **1978**, *158*, 171–180.
(26) Kapila, S.; Vogt, C. R. *HRC CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* **1981**, *4*, 233–235.
(27) Langhorst, M. L. *J. Chromatogr. Sci.* **1981**, *19*, 98–103.
(28) Cox, R. D.; Earp, R. F. *Anal. Chem.* **1982**, *54*, 2265–2270.
(29) Freedman, A. N. *J. Chromatogr.* **1980**, *190*, 263–273.
(30) Casida, M. E.; Casida, K. C. *J. Chromatogr.* **1980**, *200*, 35–45.
(31) Senum, G. I. *J. Chromatogr.* **1981**, *205*, 413–418.
(32) Freedman, A. N. *J. Chromatogr.* **1982**, *236*, 11–15.
(33) Carroll, D. I.; Dzidic, I.; Stillwell, R. N.; Horning, E. C. *Anal. Chem.* **1975**, *47*, 1956–1959.
(34) Kim, S. H.; Betty, K. R.; Karasek, F. W. *Anal. Chem.* **1978**, *50*, 1784–1788.