

Surface Ionization Ion Mobility Spectrometry

Ching Wu and Herbert H. Hill, Jr.*

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

U. Kh. Rasulev and E. G. Nazarov

Arifov Institute of Electronics, Uzbek Academy of Sciences, Akademgorodok, 700143 Tashkent, Uzbekistan

A surface ionization (SI) source was designed and constructed for ion mobility spectrometry (IMS). Compared with a conventional ^{63}Ni source, the surface ionization source is as simple and reliable, has an extended dynamic response range, is more selective in response, and does not have regulatory problems associated with radioactive ionization sources. The performance of this SI-IMS was evaluated with several different classes of compounds. Triethylamine was employed for studying the behavior of the ionization source under different source conditions and gaseous environments. Amines, tobacco alkaloids, and triazine herbicides were also investigated. Picogram level detection limits were achieved for target compounds with a response dynamic range of 5 orders of magnitude. Selective monitoring by IMS was also demonstrated. While the surface ionization source does not have the universality of response that is obtained with a ^{63}Ni ionization source, it is an excellent nonradioactive alternative for the ionization and ion mobility detection of those compounds to which it responds.

For over 20 years, radioactive ionization sources have been the ionization source of choice for ion mobility spectrometry (IMS).^{1,2} They need no power, are mounted in a manner that requires a minimum of volume and weight, and are very reliable. ^{63}Ni , the most common radioactive ionization source used in IMS, has a half-life of 100 years. Although ^{63}Ni has significant advantages, it also has serious drawbacks. Because nickel is oxidized in the atmosphere, a ^{63}Ni radioactive source must be periodically wipe-tested following Nuclear Regulatory Commission (NRC) procedures. Furthermore, manufacturing, transporting, storing, operating, and disposing hardware containing a ^{63}Ni radioactive source must follow the NRC regulations. Because of these handling problems, a nonradioactive ionization source for IMS that can replace the ^{63}Ni ionization source is highly desirable. Successful examples of nonradioactive sources for IMS using thermionic ionization,³ photoionization,⁴ laser ionization,⁵ coro-

naspray ionization,⁶ and electrospray ionization⁷ have been reported for a variety of applications.

Surface ionization of organic compounds has been studied since the 1960s.^{8,9} The phenomenon has been developed as a unique ionization method for mass spectrometry and gas chromatography for the detection of compounds with low ionization energies (most alkylamines and other nitrogen-containing compounds).^{10–13} For positive mode ionization, when analytes reach the heated ionization surface, they dissociate by losing a hydrogen atom, H, or an alkyl group, R. The remaining portion of the molecule can then be ionized to form product ions. Thus, typical product ions created by surface ionization are $(M - H)^+$ and $(M - R)^+$. At low emitter (the surface ionization source) temperatures and high analyte concentrations, the $(M + H)^+$ species can form on the surface and desorb as protonated $(M + H)^+$ ions.¹⁴ $(M + H)^+$ ions can also be produced as a result of ion–molecular reactions of $(M - H)^+$ and $(M - R)^+$ ions with original molecules in the gaseous phase. For ionization under atmospheric conditions, SI mass spectra have shown that, in addition to $(M - H)^+$, $(M - R)^+$, and $(M + H)^+$ ions, clusters of these ions with the parent molecule are possible.¹⁵

A surface ionization source offers some unique features that allow it to be used as an ionization source for IMS. First, since surface ionization does not respond to most small molecules, such as H_2O , CO_2 , CO , N_2 , and O_2 which may exist in air, no general background ions are created by this method. Second, because surface ionization does not rely on gas-phase ion–molecule reactions in its ionization process, there is no competitive distribution of the available charge among reactant ion clusters

* To whom correspondence should be submitted. E-mail: hhill@wsu.edu. Fax: (509) 335-8867.

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and analytes in the sample. Absence of interference from reactant ion clusters can provide a more quantitative response with a longer dynamic range. Finally, surface ionization is a compound-specific technique; thus, high response selectivity can be achieved.

In this study, a surface ionization (SI) source was constructed for ion mobility spectrometry. The traditional SI target compound, triethylamine, was employed to investigate the fundamental behavior of the SI-IMS system. Three groups of compounds, including nicotine and its metabolite, degradation products of chemical warfare agents, and triazine herbicides, were studied by both direct SI-IMS and GC-SI-IMS. For these different compounds, detection limits and dynamic response ranges of a GC-SI-IMS system were investigated. Selective detection of atrazine and other triazine herbicides was demonstrated.

EXPERIMENTAL SECTION

The surface ionization source was constructed in an existing IMS tube.⁷ As shown in Figure 1a, the SI emitter was mounted on a cylindrical cap at the end of the IMS drift tube. On the end cap, a 40 × 12-mm opening was made and functioned as the drift tube exit. Its position guided the drift gas so that it swept the emitter surface. Since the same potential was applied to the end cap and the emitter, it was also necessary to design a repeller plate which forced ions to move down the IMS tube. The SI emitter was made of a piece of single-crystal molybdenum, 8 mm o.d. and 38 mm in length. It has been demonstrated that the use of a single-crystal emitter can prevent degradation of the ionization surface.¹³ Before use, the emitter was conditioned at 500 °C for 15 min in O₂ flow to generate a MoO layer on the emitter surface. A schematic diagram (cross-section view) of the SI-IMS is shown in Figure 1b. The IMS drift tube was constructed of stacked stainless steel rings separated by Pyrex insulators. The stainless steel rings were connected by a series of 1-MΩ resistors. It was 11 cm in length (10 cm between the two gates) and had an inside diameter of 4.2 cm. When the drift voltage was applied to the first ring of the tube, a uniform electric field directed ions down the tube to a terminal Faraday plate, where ion current was collected and amplified. Inside the drift tube, a preheated countercurrent dry nitrogen gas was employed as drift gas. The ion gates were controlled by software developed at WSU based on the Burr-Brown PCI-20000 data acquisition/control system (Intelligent Instrumentation Inc., Tucson, AZ) on an IBM AT-compatible computer (Cactus Computer Co., Moscow, ID). The detector output was amplified and sent to the data acquisition system on the computer. Chromatograms were recorded by a HP3392A integrator (Hewlett-Packard, Wilmington, DE) after the same Keithley amplifier.

Spectra of triethylamine (Pierce Chemical Co., Rockford, IL), *N,N*-diethylethanolamine (DEEA), and 2-(diisopropylamino)ethanol (DIPAE) (Aldrich Chemical Co. Inc., Milwaukee, WI) were obtained by directly introducing diluted headspace vapor into the IMS tube. Except where specified, the instrument conditions for IMS operation were as follows: drift tube temperature, 192 °C; drift gas flow, 650 mL/min; drift range electrical field, 306 V/cm. IMS spectra were obtained in the signal-averaging mode, typically averaged 1024 times. The total sampling time was about 51 s. The entrance gate pulse width was 0.2 ms. The spectra of nicotine, cotinine (Aldrich Chemical Co. Inc., Milwaukee, WI), and triazine standards (Supelco, Inc., Bellefonte, PA) were

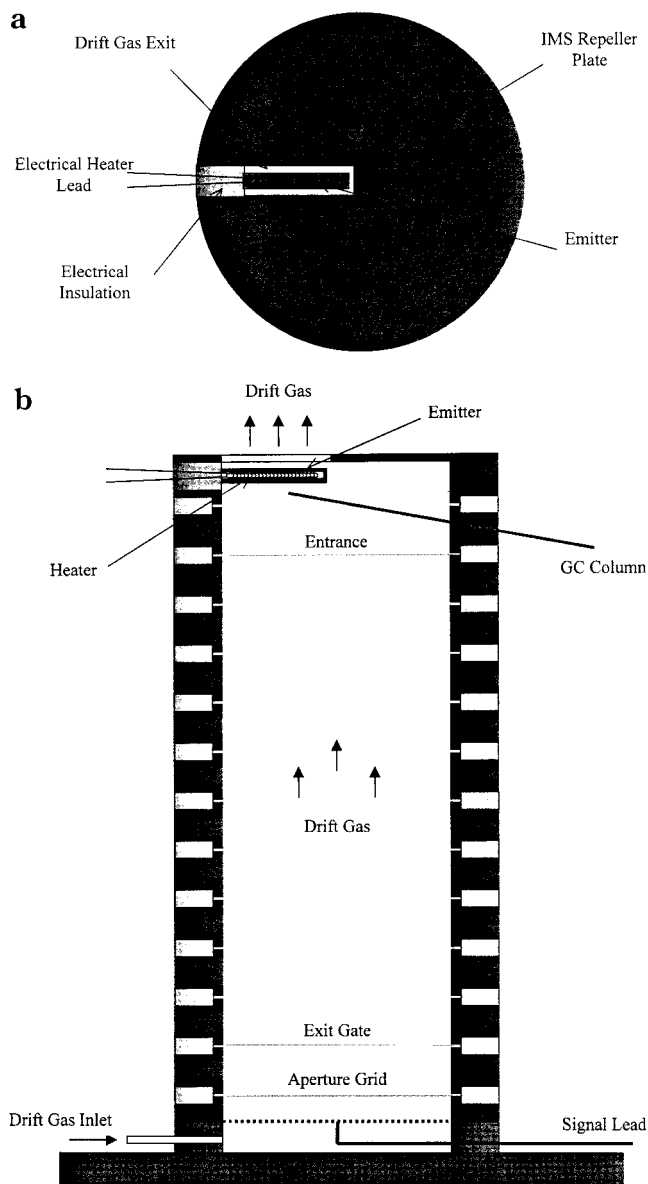


Figure 1. (a) End view of surface ionization ion mobility spectrometer. (b) Cross-sectional view of the surface ionization ion mobility spectrometer.

measured under these IMS conditions after separation by an HP 5890 gas chromatograph (Hewlett-Packard, Wilmington, DE) equipped with a DB-5ms (J&W Scientific, Folsom, CA) capillary column. The column was 0.32 i.d., 30 m in length, 0.5 μm in film thickness. A meter of 1/8-in. copper tubing was used as the transfer tubing for GC column, which was mounted on top of the GC and ended at the heated IMS oven. The tubing temperature was held constant at 250 °C. To improve the total signal intensity, when operated as a chromatographic detector in the nonselective mode, IMS gates were controlled as follows: entrance gate pulse width, 4.00 ms; exit pulse width, 4.00 ms; delay time, 11.00 ms; duty cycle, 18.25 ms. Operating conditions used for selective monitoring will be noted later for each experiment.

The temperature of the ionization surface was controlled by a dc voltage regulator (Electronics Shop, Washington State University, Pullman, WA), which was used to adjust the current of a battery-powered electrical heater. The emitter temperature was

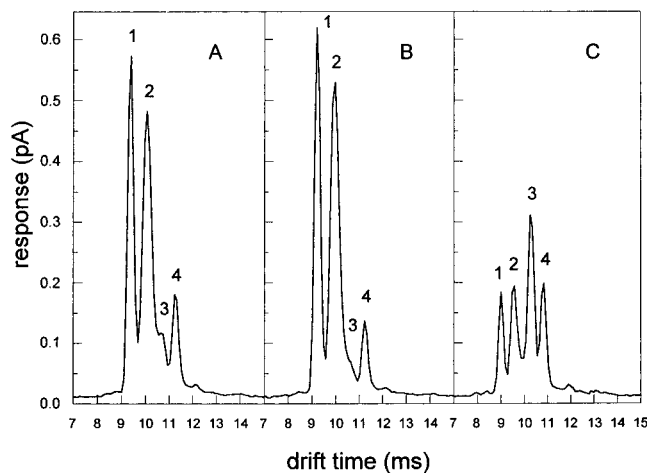


Figure 2. Ion mobility spectra of triethylamine in different gaseous environments: (A) air, (B) oxygen, (C) nitrogen. SI emitter temperature, 375 °C; IMS temperature, 192 °C.

measured by directly attaching a K-type thermocouple (Omega, Stamford, CT) onto the emitter surface. In most cases, the emitter was operated at 375 °C. For comparison, our electrospray ionization source⁷ was also evaluated in this study. For the electrospray ionization experiments, the electrospray needle was operated at 8800 V and the IMS drift voltage at 4800 V. The IMS conditions were the same as those described above. All standards used in the study were made by diluting pure chemicals with HPLC grade methanol (J. T. Baker, Phillipsburg, NJ) to ~1 mg/mL in concentration.

The ion mobility (K) data reported in this manuscript were calculated according to¹⁶

$$K = L^2 / Vt_d$$

where L is the length of ion drift region, t_d is the drift time, and V is the voltage applied across the ion drift region. By normalizing K to standard conditions, 273 °C and 760 Torr, the reduced mobility constants (K_0) were reported as the value of

$$K_0 = K(273/T)(P/760)$$

where T and P are the temperature and pressure of the drift gas.

RESULTS AND DISCUSSION

The initial investigation of surface ionization for IMS was conducted with triethylamine as the test compound. Spectra shown in Figure 2 compare the SI-IMS responses for triethylamine in three different drift gases: air, oxygen, and nitrogen. The IMS spectra were obtained after conditioning the emitter surface with the respective drift gas for 30 min. Triethylamine vapor was directly introduced into the IMS tube by a 10-mL gastight syringe. Four major product ion peaks were observed from the surface ionization of triethylamine in nitrogen. For both oxygen and air, product ion peak 3 was reduced in intensity, but the overall ion current was 3 times higher than that in nitrogen. Oxygen is thought to modify the surface, improving ionization efficiency by

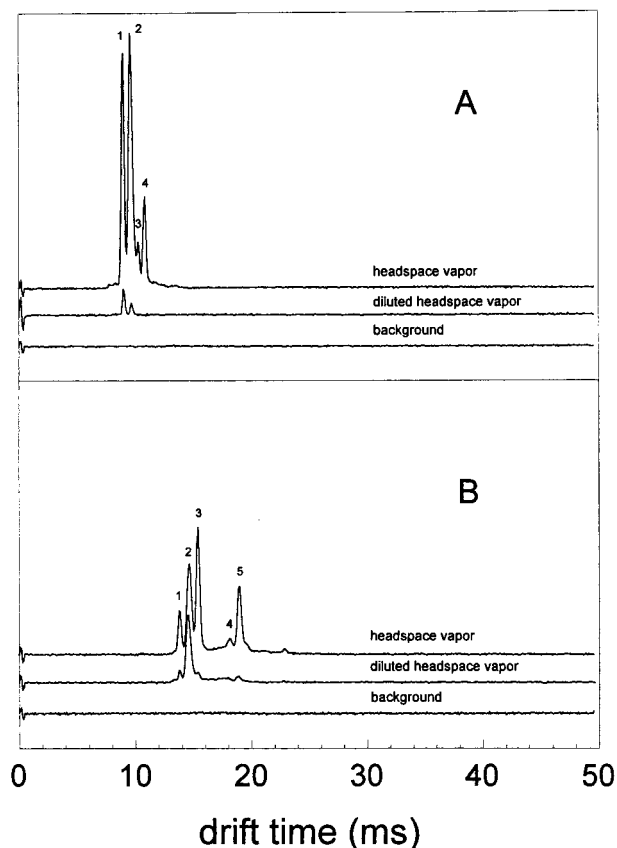


Figure 3. Characteristic ions formed on the MoO surface of triethylamine. Emitter temperature, 375 °C; IMS tube temperature, (A) 192 and (B) 32 °C.

changing the work function of the surface.⁹ Pure oxygen, however, decreased the useful lifetime of the emitter by increasing the surface oxidation rate. Thus, air was chosen for the drift gas used in this work. Not only was air found to be the best choice based on ionization efficiency and lifetime considerations, but for application as a field portable device, air has the practical advantage of availability. Adequate filtering permits the use of ambient air from the field, eliminating the need to transport high-pressure gas tanks to the analysis site.

Figure 3 demonstrates the ion species formed on the ionization surface under different sample concentrations and IMS tube temperature conditions. In Figure 3a, when large amounts (~100 ppm) of sample were injected, four major peaks were observed. When the injected amount was about 1/125 of the original, there were only two peaks. Mass spectrometric studies have demonstrated that major product ions formed on MoO emitters will be $(M - H)^+$ and $(M - R)^+$. From the figure, no peak was observed in the background spectra when triethylamine was absent, while two peaks were observed when low concentrations (<1 ppm) of triethylamine were introduced into the detector; therefore, peak 1 at a drift time of 9.00 ms ($K_0 = 2.15 \text{ cm}^2/(\text{V}\cdot\text{s})$) was assigned to the $(M - R)^+$ and peak 2 at drift time 9.58 ms ($K_0 = 2.02 \text{ cm}^2/(\text{V}\cdot\text{s})$) to $(M - H)^+$. Compared with $(M - H)^+$, $(M - R)^+$ was smaller and would have a higher ion mobility.¹⁶ At the lower IMS tube temperature (32 °C), shown in Figure 3b, ion mobility spectra were clearly different than those at high IMS temperatures (192 °C) shown in Figure 3a. The third peak was dominant at high concentrations and almost disappeared at low concentrations. This

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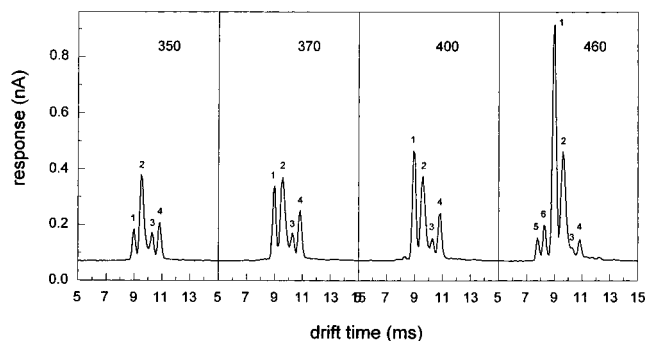


Figure 4. High-temperature ion mobility spectra of triethylamine at different emitter temperatures. IMS temperature, 192 °C; emitter temperature, 350, 370, 400, and 460 °C.

matched the expected behavior of $(M + H)^+$. Under common surface ionization conditions, it has been suggested that $(M + H)^+$ is formed by a bimolecular reaction on the emitter surface as a result of the interaction of $(M - H)^+$ and $(M - R)^+$ ions with a molecule, M , in the gaseous phase.¹⁵ Clearly, these reactions are more favorable under condition of high sample concentration.

Triethylamine has also been studied by conventional ^{63}Ni ionization IMS.¹⁷ Its product ion is known to be the $(M + H)^+$ ion, with a reduced mobility of $1.95 \text{ cm}^2/(\text{V}\cdot\text{s})$. The reduced mobility for the third peak from the surface ionization spectra was $1.93 \text{ cm}^2/(\text{V}\cdot\text{s})$, which matched well with the literature value expected for $(M + H)^+$. Thus, the third peak was identified as $(M + H)^+$.

The measured reduced mobilities for peaks observed in the high IMS temperature spectra were 2.15, 2.02, 1.90, and $1.87 \text{ cm}^2/(\text{V}\cdot\text{s})$ and were 2.15, 2.02, 1.93, 1.64, and $1.56 \text{ cm}^2/(\text{V}\cdot\text{s})$ for the low IMS temperature spectra. Comparing these two groups of mobility data, the first and second peaks were identical; the third peak shifted to a high mobility value in the low IMS temperature spectrum, which might have been caused by interference from the unresolved $(M - H)^+$ peak. Peaks with ion mobilities of 1.64 and $1.56 \text{ cm}^2/(\text{V}\cdot\text{s})$, observed in the low-temperature IMS spectra, were cluster ions formed in the gas phase close to the emitter surface. These cluster ions, such as $(M_n - H)^+$ and $(M_n - R)^+$, have also been found in mass spectrometric studies.⁹

As shown in Figure 4, the spectra obtained under the highest emitter temperature condition (460 °C) contained two ion species which moved faster than triethylamine-related ions. These ions came from an elemental impurity of the emitter, namely the alkali metal atoms Na and K which had previously been observed emitting from the surface.⁹ These atoms diffused from the emitter bulk toward to the surface and became ionized at the surface with 100% efficiency. They were found as background ions at high emitter temperatures, and their intensity increased with increasing emitter temperature. In addition, the signal intensities of $(M - H)^+$ and $(M - R)^+$ were found to depend on the ionization surface temperature,⁹ as demonstrated in Figure 4.

The temperature dependence of ion current corresponding to triethylamine product ions and instrument noise level was also studied. In comparison to the surface ionization detector (SID),¹⁸ the trends of product ion and background ion current change with

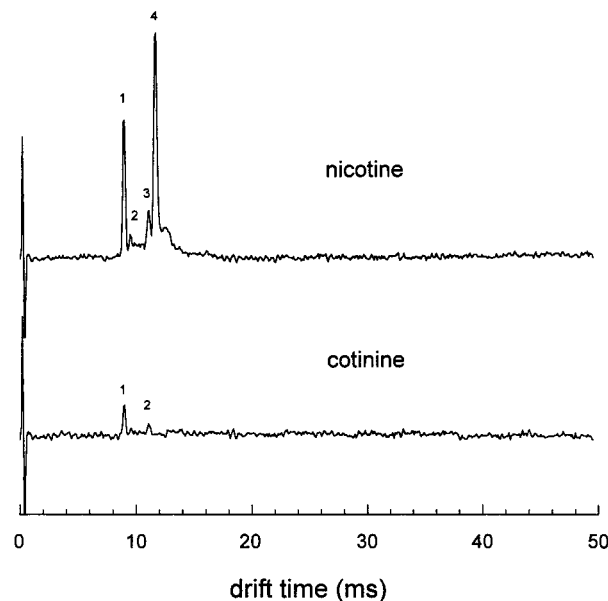


Figure 5. Ion mobility spectra of nicotine and cotinine. GC conditions: oven temperature, 200 °C; injector temperature, 250 °C; injection quantity, 1 μL of 1 $\mu\text{g}/\mu\text{L}$ nicotine; 0.3 μL of 10 $\mu\text{g}/\mu\text{L}$ cotinine.

temperature were similar to SID data. Nevertheless, there was no significant change of detector noise level when emitter temperature was elevated. This suggested that emitter can be operated at relatively higher temperatures to improve the signal-to-noise ratio. However, the operating temperature must be controlled in order to achieve a reproducible response. As observed in this experiment, at 450 °C, the response of triethylamine kept increasing. High emitter temperature may accelerate oxidation reactions on the emitter surface, increasing MoO surface area and leading to irreproducible response.

Surprisingly, decreasing the IMS tube temperature did not decrease the IMS resolution. Presumably, this was because the surface ionization method was specific for target compounds, and no complicated water clusters or other interferences were created during ionization. Thus, low-temperature IMS could be applied to selective detection of amine type compounds in the field. SI-IMS is suitable as a field monitoring device not only because it is not radioactive but also because it can be operated at ambient temperature. Moreover, since the surface ionization process does not rely on gas-phase ion-molecule reactions, the reaction region of a conventional IMS tube is no longer necessary, and the size of an IMS tube can be reduced about 30%.

Figure 5 shows the characteristic product ions of nicotine and cotinine created by the surface ionization method. Four major peaks with reduced mobilities of 2.14, 2.04, 1.73, and $1.65 \text{ cm}^2/(\text{V}\cdot\text{s})$ for nicotine and two peaks with reduced mobilities of 2.14 and $1.75 \text{ cm}^2/(\text{V}\cdot\text{s})$ for cotinine were obtained. Two of the ion species had identical reduced ion mobilities. However, the ionization efficiency of cotinine was about 1.4% that of nicotine (efficiency was calculated from total ion current when the same sample size was injected). Cotinine is a major metabolite of nicotine, produced by 5' carbon oxidation. It has been demonstrated that surface ionization is a structure-specific ionization method.⁹ This selectivity for nicotine corresponded to the ionization energy difference before and after oxidation.

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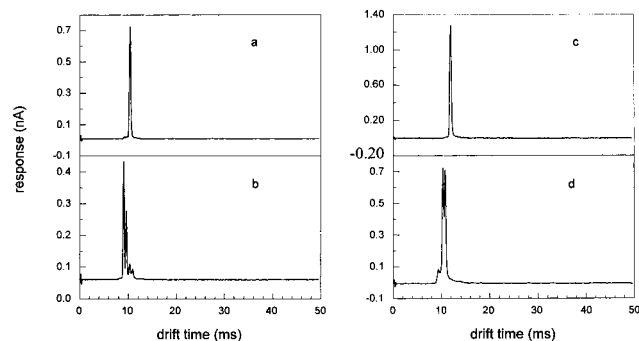


Figure 6. Comparison of ion mobility spectra of electrospray ionization and surface ionization. IMS temperature, 192 °C; emitter temperature, 375 °C; ESI source, needle potential at 8800 V, drift potential 4800 V. (a) Surface ionization, 2-(diisopropylamino)ethanol; (b) surface ionization, *N,N*-diethylethanolamine; (c) electrospray ionization, 2-(diisopropylamino)ethanol; (d) electrospray ionization, *N,N*-diethylethanolamine.

In addition to ionization, selective response to nicotine can be obtained by monitoring certain ion species which have a distinctive ion mobility. For example, peak 4, with a reduced mobility of $1.65 \text{ cm}^2/(\text{V}\cdot\text{s})$, was unique in the nicotine spectrum and was used for selective detection. Numerous GC methods have been applied for detection of nicotine and cotinine in human fluids.^{19,20} However, none of them, including NPD and GC/MS, provides both compound-specific ionization and selective monitoring to discriminate between nicotine and its metabolites. The GC-SI-IMS can be an ideal choice for selective nicotine detection in a complex matrix.

A calibration curve for nicotine had a linear dynamic response over 4 orders of magnitude with a slope of 0.8 on a log–log plot. The detection limit was determined to be $2.2 \times 10^{-13} \text{ g/s}$. This result was similar to the detection limit obtained by IMS with a conventional ^{63}Ni ionization source.²¹ Under the chromatographic conditions used to achieve a calibration curve in this study, the solvent (methanol) coeluted with nicotine. No significant effect on signal intensity was observed when the solvent was eluted with analyte.

Other examples of compounds detected by SI-IMS were 2-(diisopropylamino)ethanol (DIPAE) and *N,N*-diethylethanolamine (DEEA), major degradation products of VX- or V-type chemical warfare agents. Currently, they are primarily analyzed by GC/MS methods. Figure 6 shows the ion mobility spectra of DIPAE and DEEA by both surface ionization (SI) and electrospray ionization (ESI) IMS. Figure 6a and c are ion mobility spectra of DIPAE by SI and ESI, respectively. Even though there was only one dominant product ion observed in both spectra, different reduced mobilities (1.65 for ESI, 1.89 for SI) indicated that different ion species were formed by the two methods. Similarly, Figure 6b and 6d are ion mobility spectra of DEEA by SI and ESI, respectively. In Figure 6d, the first and second peaks were from the electrosprayed solvent, determined from solvent blank,

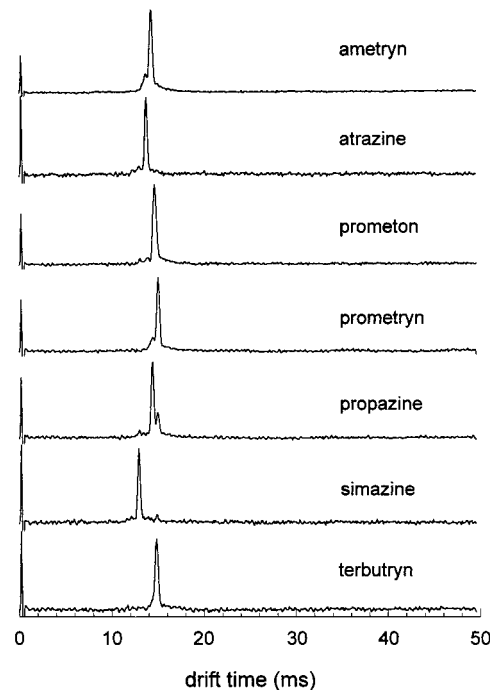


Figure 7. Ion mobility spectra of triazine herbicides. GC conditions: oven temperature, 200 °C; injector temperature, 250 °C; injection quantity, 1 μL of 1 $\mu\text{g}/\mu\text{L}$ samples.

while the third peak corresponded to DEEA with a reduced mobility of $1.83 \text{ cm}^2/(\text{V}\cdot\text{s})$. In surface ionization ion mobility spectra, Figure 6b, multiple peaks with reduced mobilities of 2.14, 2.00, 1.88, and $1.78 \text{ cm}^2/(\text{V}\cdot\text{s})$ were observed. As mentioned above, no reactant or solvent ions are observed in surface ionization spectra. All of these four peaks were product ions of DEEA.

Since surface ionization does not rely on the gas-phase proton-transfer reactions and is free from many forms of chemical interferences, better quantitative data can be expected than those possible from the ^{63}Ni source. For both DIPAE and DEEA, dynamic response ranges were over 5 orders of magnitude. The slope was 0.95 for DEEA and 0.87 for DIPAE. The calculated detection limit was $3.7 \times 10^{-14} \text{ g/s}$ for DEEA and $3.9 \times 10^{-14} \text{ g/s}$ for DIPAE.

A third example of an application for SI-IMS is the determination of triazine herbicides. Triazine herbicides are among the most commonly used to inhibit broadleaf weeds for both agricultural and nonagricultural purposes. They are normally analyzed by GC/MS methods.^{22,23} The maximum allowable concentration of an individual pesticide in drinking water is 0.1 ppb according to European Commission Regulations. In this part of the study, seven triazine compounds were investigated: ametryn, atrazine, prometon, prometryn, propazine, simazine, and terbutryn. All contained a triazine ring, but with different alkyl groups attached. Since they all contain one or two secondary amino groups, SI-IMS should be a sensitive detection method for this class of compounds. The ion mobility spectrum of each compound is shown in Figure 7. The reduced mobilities, in $\text{cm}^2/(\text{V}\cdot\text{s})$, were

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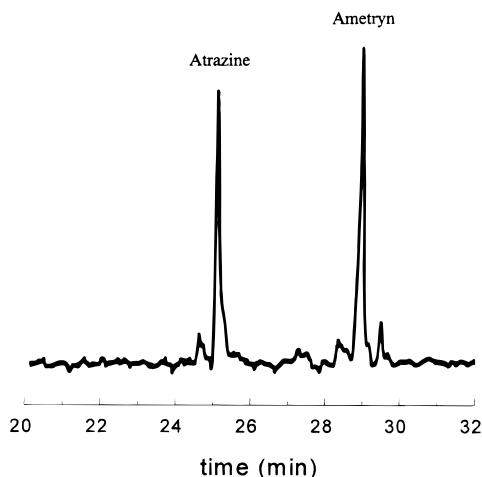


Figure 8. Gas chromatogram of triazine herbicide mixture detected by selective mode surface ionization ion mobility spectrometry. GC conditions: oven temperature, 50 °C for 1 min, 25 °C/min to 175 °C, 5 °C/min to 250 °C for 10 min; injector temperature, 300 °C; injection quantity, 1 μ L of 0.01 μ g/ μ L sample.

1.42, 1.36 for ametryn; 1.41 for atrazine; 1.33 for prometon; 1.29, 1.34 for propazine; 1.29, 1.34 for simazine; and 1.29, 1.50, 1.31 for terbutryn.

Figure 8 shows a selective IMS tracing obtained after gas chromatographic separation of a mixture of these triazines. In this chromatogram, the IMS was tuned to monitor only ions with a mobility of 1.41, providing a selective response for atrazine and ametryn. The elution order of these two compounds was verified with single standard injections.

CONCLUSIONS

As a new ionization source for IMS, surface ionization can be employed for the detection of compounds with low ionization energies. Amines (including degradation products of chemical warfare agents), tobacco alkaloids, and triazine herbicides are examples of compounds that can be detected by SI-IMS. Surface ionization has most of the positive features of a conventional ^{63}Ni source, such as simplicity and reliability. With respect to handling and maintenance, however, surface ionization avoids many of the difficulties encountered with the ^{63}Ni source. The dynamic range is several orders of magnitude greater than that of the ^{63}Ni source, and since the surface ionization process does not involve gas-phase ion–molecule reactions, the IMS tube can be constructed without a “reaction region”, reducing the length of the tube by 30%. In addition, the IMS can be operated at low temperature

Table 1. Mass Identification of Ions Formed by Atmospheric Pressure Surface Ionization of Triethylamine

m/z	relative intensity	identity
86	41	$(\text{M} - \text{CH}_3)^+$
87	2.7	$(\text{M} - \text{CH}_3 + 1)^+$
98	4.6	
100	12	$(\text{M} - \text{H})^+$
102	100	$(\text{M} + \text{H})^+$
103	7.6	$(\text{M} + \text{H} + 1)^+$
112	9.9	
120	3.3	$(\text{M} + \text{H}_2\text{O} + \text{H})^+$

without suffering interference from cluster ions that often cause resolution loss in the IMS. The tradeoff, of course, is that the SI-IMS is a selective detector, while ^{63}Ni -IMS is a universal detection method.

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APPENDIX

Table 1 reports mass identification of ion species formed in the SI source used in the IMS experiments for the triethylamine standard. The mass spectrometric data were obtained by an IMS/MS system constructed in our laboratory.²⁴ Ions formed in the ionization source were guided by an electric field toward a pinhole leak, which served as the interface between the SI source and the MS. A detailed description of the interface design can be found in ref 24.

Mass spectrometric information shown in Table 1 demonstrate that $(\text{M} - \text{H}/\text{R})^+$ ions formed in the SI source were stable under atmospheric conditions. Note that in this experiment, triethylamine was continuously introduced into the IMS with the drift gas flow. As stated in the text, considerable gas-phase ion–molecular reactions between $(\text{M} - \text{H}/\text{R})^+$ and their precursors may result in the formation of $(\text{M} + \text{H})^+$. In addition, the ion distribution observed in the mass spectrometer may not be representative of that at atmospheric pressure due to charge-stripping, charge-transfer, or ion–molecule reactions at the IMS/MS interface.¹⁸ Nevertheless, the observation of intense $(\text{M} - \text{H}/\text{R})^+$ ions in the mass spectrum strongly supported the conclusions from IMS study based on observed mobilities described in this manuscript.

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