Evaluation of Sulfonylurea Herbicides Using High Resolution Electrospray Ionization Ion Mobility Quadrupole Mass Spectrometry

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Abstract: The purpose of the current study was to explore and assess the potential of high resolution electrospray ionization atmospheric pressure ion mobility spectrometry (ESI–AP-IMS) as a field analytical method for the detection and identification of mixtures of sulfonylurea (SU) herbicides in aqueous samples. Because of increased usage, persistent behavior, and potential for crop damage, an environmental method of analysis capable of evaluating SU herbicides in a swift and effective manner is necessary. Eight SU herbicides were evaluated using ESI–AP-IMS quadrupole mass spectrometry. The selected herbicides were chosen based upon availability and scope of use. The SU herbicide species were qualitatively identified using quadrupole mass spectrometry, followed by the determination of reduced mobility values for characteristic ions. Various mixtures of rimsulfuron, metsulfuron-methyl, prosulfuron, sulfometuron-methyl, tribenuron-methyl, and primisulfuron-methyl could be revealed using AP-IMS. The ease of use, ability to operate under ambient conditions, and relatively rapid data acquisition times make ESI–AP-IMS an attractive candidate for the analysis of aqueous environmental field samples. © 2002 Wiley Periodicals, Inc. Field Anal. Chem. Technol. 5: 302–312, 2001; DOI 10.1002/fact.10010

Keywords: Ion Mobility Spectrometry (IMS); Electrospray Ionizations (ESI); pesticides; sulfonylurea; herbicides

Introduction

Sulfonylurea (SU) herbicides inhibit acetolactate synthase (ALS), the enzyme which is fundamental for the synthesis of branched chain amino acids (i.e., valine, leucine, and isoleucine). While the inhibition of this enzyme is extremely efficient in broad-leaf plants, toxicity in mammals is quite low.1 Preliminary studies on various mammalian species indicate a low degree of carcinogenicity; however, SU herbicides have been shown to adversely affect aquatic systems, specifically, algae populations.2 Despite relatively low applications rates, the increased usage of SU herbicides has allowed for certain species to develop a limited resistance to traditional SU mixtures.3 To combat this behavior, SU herbicides must be applied in greater quantity to achieve the desired effect. Consequently, an increased environmental concentration is expected. Environmentally, SU herbicides are relatively insoluble in aqueous systems and demonstrate a high degree of stability under alkaline soil conditions.5 Residual SU herbicides have shown the capacity to endanger future nontarget rotational crops by decreasing crop and seed yield.6 While the potential human risks associated with SU herbicide exposure is negligible, data concerning chronic environmental effects of SU application is not available. The lack of data concerning the long-term environmental fate of SU herbicides and the potential risks associated with prior SU application requires the development of a rapid screening method for SU herbicides in the environment. Traditional methods of analysis for SU herbicides include HPLC,7–9 LC–MS,10–12 immunoassay,7,9 capillary electrophoresis,11 and gas chromatography13 with derivitization.

Aside from immunoassay techniques, the traditional methods of SU herbicide detection are limited to a laboratory setting. Atmospheric pressure ion mobility spectrometry
(AP-IMS) fitted with a modified electrospray ionization (ESI) source offers an alternative method capable of directly analyzing aqueous samples for polar organic molecules. Rapid data acquisition times and minimal sample preparation make this technique an attractive candidate for field analysis of aqueous samples. Ion mobility has traditionally been used in gas-phase monitoring systems; however, it has not until recently been applied to aqueous samples. With the adaptation of ESI technology to operate under high temperature, the range of application for IMS has greatly increased.

Electrospray ionization AP-IMS quadrupole mass spectrometry (ESI–AP-IMS–QMS) provides a comparatively rapid method for the detection of a wide variety of compounds using a two-dimensional (size/charge and mass/charge) data acquisition system. While ESI–AP-IMS–QMS has received considerable attention for the rapid screening of illicit drugs, chemical warfare agents, explosives, and peptides, it has received little consideration as a viable aquatic environmental analytical technique. Coupling of ESI with IMS–MS circumvents the necessity of excessive sample preparation, as filtered water samples may be directly sprayed into the instrument. In addition to functioning as a means for detection, the quadrupole mass filter aids in the acquisition of mobilities by selecting specific ions or a range of ions for analysis. This feature of QMS allows for the elimination of common interfering ions.

**Experimental Section**

**Materials**

Standards, specifically prosulfuron, tribenuron, metsulfuron-methyl, theifensulfuron-methyl, primisulfuron-methyl, rimsulfuron, triasulfuron, and sulfometuron-methyl were obtained from Supelco and ChemService, while the HPLC grade solvents were acquired from Fischer Scientific. Each standard was dissolved in acetonitrile and diluted with a 50:50 mixture of water and ACN. From these 25 µg/ml stock solutions, diluted individual standards along with herbicide mixtures were created.

**ESI**

To ensure the efficient desolvation of analyte ions, the temperature of the drift tube was held at 200°C. This high temperature region is typically not a favorable environment for the proper function of traditional electrospray sources. Thermal factors may affect the needle operation in a negative fashion; therefore, a cooled electrospray source is needed to minimize corona discharge and eliminate solvent evaporation within the needle.23 The design and assembly of the cooled ESI source used in this experiment were conducted in our laboratory. The ion source is constructed out of a hollow, cylindrical Teflon sheath, a smaller diameter alumina tube, and the electrospray needle. The hollow Teflon sheath of the unit functions to allow water-cooling to occur, while the alumina tube serves as an electrical insulator between the water and the needle. Additionally, a gas inlet was incorporated into the design to provide a bath gas around the needle. The electrospray unit is approximately 35 mm in diameter and 70 mm in length. A schematic of the ESI source is shown in Fig. 1. The needle voltage was held constant at 13.5 kV. Samples were introduced using a 70-µl sample loop with a standard LC injection port. Running at 5 µl/min (50:50 ACN:water), the Brownlee Labs (Santa Clara, CA) LC pump allowed for a sample to be analyzed for approximately 14 min before the next sample must be injected.

**Atmospheric Pressure Ion Mobility Quadrupole Mass Spectrometer**

The ion mobility spectrometer designed and constructed by Hill et al. employed a stacked ring design and has been described previously in detail.24 The key components of the system included the ESI source, desolvation region, drift region, interface and quadrupole mass spectrometer. The ion mobility tube consisted of a series of alternating insulating and conducting rings. A voltage potential of 9.9 kV (7.85 kV at the ion gate) was applied to the system, resulting in an electric field of approximately 350 V/cm. The electric field gradient was created by a series of 500 kΩ (desolvation region) and 1 MΩ (drift region) resistors joining the individual stainless steel conducting rings. A schematic of the system is shown in Fig. 2. Samples introduced into the desolvation region at 200°C were gated into the drift region and mass spectrometer using a Bradbury–Nielsen ion gate. Unwanted neutral molecules and particulate matter were swept out of the IMS tube by a countercurrent flow (800 ml/min) of heated nitrogen gas. Sample ions entered the C150-Q quadrupole (ABB Extrel, Pittsburgh, PA) mass spectrometer through a 40-µm aperture. The quadrupole mass filter was an arrangement of four 0.95 cm diameter rods 20 cm in length. The

![FIG. 1. The ESI source consists of a Teflon casing which houses the needle and electrically isolates the system. The alumina tube serves as an electric barrier between the cooling bath and ESI needle. The needle must be cooled to prevent solvent evaporation and needle degradation under high temperature.](Image)
Experimental Determination of Reduced Mobility Constants

The experimental measurement of ion mobility requires a mechanism for recording ion drift time, \( t_d \), through a mobility tube of length \( L \). The drift time of an ion is a function of the drift region length, applied potential, \( V \), and the ion mobility constant of proportionality, \( K \) (cm²/V s). The relationship between drift time, applied potential, and the ion mobility constant of proportionality is as follows:26,27

\[
t_d = \frac{L^2}{KV}
\]  

(1)

As parameters between experiments and instruments vary so do drift times for the same analyte ions. To circumvent the obvious problems with reporting drift times, an experimentally determined reduced mobility constant, \( K_0 \), is used for ion identification using IMS. The value of \( K_0 \) (cm²/V s) is obtained by standardizing the experimental ion mobility value, \( K \), for pressure and temperature, as in the following:26,27

\[
K_0 = \left( \frac{L^2}{Vt_d} \right) \left( \frac{273.15}{T} \right) \left( \frac{P}{760} \right)
\]

(2)

Equation (2) incorporates the drift tube length, \( L \), gate voltage, \( V \), drift time, \( t_d \), temperature, \( T \), in Kelvin, and pressure, \( P \), in Torr. In any given ion mobility experiment the ion drift time, \( t_d \), is the experimentally determined value, while all other values in the determination of a reduced mobility value are constant.

Results and Discussion

SU Herbicide Analysis

Eight SU herbicides were evaluated using ESI–AP–IMS–QMS. The individual SU ions were evaluated using both ion mobility and mass spectrometric methods. Table 2 lists the most commonly seen SU herbicide ions along with their corresponding \( m/z \) and reduced mobility values. While ESI often forms \( [M+H]^+ \) ions, assessment of the SU herbicide standards indicated that SU species often form molecular ion adducts with sodium and potassium in addition to \( [M+H]^+ \) ions. The ion mobility spectrum of thifensulfuron-methyl, shown in Fig. 3, demonstrates this occurrence. Using the SIM capability of the QMS, the two peaks found in the ion mobility domain were identified by \( m/z \) as the \( [M+H]^+ \) \( (m/z \ 388) \) and \( [M+Na]^+ \) \( (m/z \ 410) \) species. The individual spectra, 3a and 3b, represents the ion mobility of the individual

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TABLE 1. Operating parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drift gas flow rate</td>
<td>800 ml/min (N₂)</td>
</tr>
<tr>
<td>Sample flow rate</td>
<td>5 µl/min (50:50 ACN:water)</td>
</tr>
<tr>
<td>ESI potential</td>
<td>13.5 kV</td>
</tr>
<tr>
<td>Drift tube potential</td>
<td>9.9 kV</td>
</tr>
<tr>
<td>Ion gate potential</td>
<td>7.85 kV</td>
</tr>
<tr>
<td>Drift field</td>
<td>350 V/cm</td>
</tr>
<tr>
<td>Ion lens potentials</td>
<td>28.0, −42.8, −85.7, −34.5, −17.3, and −50.9 V</td>
</tr>
<tr>
<td>Number of IMS averages</td>
<td>1000</td>
</tr>
<tr>
<td>Number of points per mobility spectrum</td>
<td>1000</td>
</tr>
<tr>
<td>Scan time</td>
<td>50 ms</td>
</tr>
<tr>
<td>Gate pulse width</td>
<td>0.2 ms</td>
</tr>
<tr>
<td>Drift tube temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Ambient pressure</td>
<td>696 Torr</td>
</tr>
<tr>
<td>Chamber pressures</td>
<td>( 1.3 \times 10^{-5} ) Torr; ( 2.0 \times 10^{-4} ) Torr</td>
</tr>
</tbody>
</table>

---

TABLE 2. SU herbicide analysis

<table>
<thead>
<tr>
<th>SU herbicide</th>
<th>( m/z )</th>
<th>Drift time (ms)</th>
<th>( K_0 ) (cm²/V s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfometuron-methyl (H⁺)</td>
<td>365</td>
<td>34.45</td>
<td>0.961</td>
</tr>
<tr>
<td>Prosfurfuron (H⁺)</td>
<td>420</td>
<td>35.55</td>
<td>0.931</td>
</tr>
<tr>
<td>Methylsulfuron-methyl (H⁺)</td>
<td>382</td>
<td>34.15</td>
<td>0.970</td>
</tr>
<tr>
<td>Methylsulfuron-methyl (Na⁺)</td>
<td>404</td>
<td>36.55</td>
<td>0.906</td>
</tr>
<tr>
<td>Triasulfuron (H⁺)</td>
<td>402</td>
<td>35.35</td>
<td>0.937</td>
</tr>
<tr>
<td>Triasulfuron (Na⁺)</td>
<td>424</td>
<td>37.40</td>
<td>0.885</td>
</tr>
<tr>
<td>Rimulsulfuron (Na⁺)</td>
<td>454</td>
<td>38.30</td>
<td>0.865</td>
</tr>
<tr>
<td>Tribenuron-methyl (H⁺)</td>
<td>396</td>
<td>33.47</td>
<td>0.990</td>
</tr>
<tr>
<td>Tribenuron-methyl (Na⁺)</td>
<td>418</td>
<td>35.20</td>
<td>0.941</td>
</tr>
<tr>
<td>Primisulfuron-methyl (H⁺)</td>
<td>469</td>
<td>37.95</td>
<td>0.873</td>
</tr>
<tr>
<td>Primisulfuron-methyl (Na⁺)</td>
<td>491</td>
<td>39.55</td>
<td>0.837</td>
</tr>
<tr>
<td>Thifensulfuron-methyl (H⁺)</td>
<td>388</td>
<td>34.70</td>
<td>0.954</td>
</tr>
<tr>
<td>Thifensulfuron-methyl (Na⁺)</td>
<td>410</td>
<td>37.20</td>
<td>0.890</td>
</tr>
</tbody>
</table>
ions contributing to the overall ion mobility spectrum. Figure 4 further illustrates occurrence of adduct formation when examining SU herbicide ions. This series of spectra represent the ion mobility spectrum of primisulfuron-methyl. In addition to [M + H]$^+$ ($m/z$ 469) and [M + Na]$^+$ ($m/z$ 491) species, a [M + K]$^+$ ($m/z$ 507) ion was seen. While common (this is not always the case) under differing experimental conditions, the degree of adduct formation can be varied. The formation of adduct ions in the electrospray process indicates the potential difficulty in identification of an individual species within a complex mixture. Given trace quantities of sodium and potassium in the experimental system, adduct formation with these atoms is unavoidable and unpredictable. Nevertheless, these sodium and potassium adducts must be accounted for during an experiment. A more comprehensive description of sodium and potassium adduct formation using ESI may be found in the work of Fenn et al.

**Experimental Determination of Resolving Power**

In order to develop an elementary understanding of the separation characteristics of SU herbicide separation, a composite plot relating reduced mobility value and $m/z$ of eight SU ions was constructed, as shown in Fig. 5. This plot...
indicates that certain SU ion species in a mixture may interfere with each other as they possess similar masses or reduced mobility values. To further investigate the capacity of the system to separate SU ions within a mixture, the resolving power of the instrument was examined.

Resolving power in ion mobility is defined as the drift time, $t_d$, of an ion divided by the peak width at half height, $w_{1/2}$, expressed in units of time.\(^{30}\)

$$R_p = \frac{t_d}{w_{1/2}}$$  \hspace{1cm} (3)

This measure of separation power as defined for ion mobility in chromatographic terms may be related to the number of theoretical plates, $N$, in the system\(^{31}\):

$$N = 5.55 \left( \frac{t_d}{w_{1/2}} \right)^2$$  \hspace{1cm} (4)

Ion migration through an ion mobility drift tube is a function of random and directed diffusion. Random diffusion is defined as the radial diffusion of an ion cloud, whereas directed diffusion is used to describe the induced movement of ions down an electric field gradient. Theoretically, the peak width observed using ion mobility techniques is a combination of the initial ion pulse width and the random diffusion of ions. These two terms are related to the theoretical minimum
FIG. 5. The composite separation of the most prominent ions formed for eight SU herbicides. This plot demonstrates the theoretical capability of the system to separate SU mixtures. All ions shown correspond to either the \([M + H]^+\) or the \([M + Na]^+\) formed by SU herbicides within the system. As many SU ions possess either similar drift characteristics or \(m/z\) values, analysis of mixtures require high resolution capabilities for comprehensive identification.

peak width at half height by the expression developed by Revercomb and Mason,

\[
w_{1/2}^2 = t_g^2 + \left( \frac{16 k T \ln 2}{V e z} \right) t_g^2
\]

where \(k\) is Boltzmann’s constant, \(T\) the temperature of the system in Kelvin, \(V\) the voltage applied across the drift region, \(e\) the elementary charge, \(z\) the number of charges attributed to an ion, and \(t_g\) the initial ion pulse width in units of time. Using this expression the experimental peak width can be compared to the theoretical minimum for a given system. Figure 6 represents a ion mobility spectrum of the \([M + H]^+\) thifensulfuron-methyl ion obtained using the SIM capability of the QMS. The centroid of peak is located at 34.7 ms with a peak width at half height of 0.34 ms. Applying Eq. (3) yields a resolving power of 102, which corresponds to approximately 58,000 theoretical plates. Comparatively, this value is midway between the separation capacities of LC and capillary GC columns. When ignoring the effects of the initial gate pulse width, the standard resolving power obtained during this experiment differed from the theoretical maximum by approximately 10%. However, when both the initial pulse width and diffusion are accounted for, the experimental resolving power differed by less than 1%. In the case of an ion mobility tube operated under low resolution conditions \((R_p = 20)\) the ions presented in Fig. 4 would be indistinguishable. Assuming that the resolving power of the system remains constant \((R_p = 20)\) over the drift range in Fig. 4, the peak widths at half maximum are 1.90, 1.98, and 2.03 ms respectively \([Eq. (3)]\).

As shown in the spectrum, the difference between the first two ions was 1.6 ms. Given the peak widths at half maximum for an \(R_p\) value of 20, the first two species in Fig. 4 would significantly overlap, as drift times differing by more than 1.94 ms \((1.90/2 + 1.98/2)\) would be required to clearly identify each of these peaks. As the first two ions would not be conclusively resolved with an \(R_p\) value of 20, it follows that the third peak, which differed from the \([M + Na]^+\) by less 1.6 ms, would be absorbed into the \([M + Na]^+\) species.

Mixture Analysis

Mixtures of SU herbicides were evaluated in the identical manner as described for the standard solutions. To identify all the constituents within SU mixtures the QMS was scanned to isolate all ions seen when analyzing the SU herbicides individually. The first mixture examined consisted of three SU herbicides, rimsulfuron, metsulfuron-methyl, and primisulfuron-methyl. Figure 7 illustrates the ion mobility separation of these three species. The three most prominent
FIG. 7. This series of spectra represent a mixture of rimsulfuron, metsulfuron-methyl, and primisulfuron-methyl. The primary spectrum containing three prominent peaks illustrates the separation of three species within the mixture. However, mass identification of ions indicates that the complete ion mobility spectrum is composed of four different SU ions: (a) corresponds to the protonated metsulfuron ion; (b) the SIM spectrum of the sodiated rimsulfuron species; (c) and (d) combine to create peak #3 within the ion mobility spectrum. These two peaks correspond to the protonated primisulfuron ion and the sodiated metsulfuron ion, respectively. This figure illustrates the necessity of the mass identification for the determination of ion mobility peaks with certain mixtures.
peaks shown in the primary spectrum correspond to the individual SU ions. The first peak in the spectrum corresponded to the protonated metsulfuron-methyl ion (m/z 382), while the second peak of the ion mobility mixture spectrum was created by the sodiated rimsulfuron species (m/z 454). Initial impressions of the ion mobility spectrum were misleading as the spectrum was a composite of four different SU ions rather than three. Further investigation indicated that the third peak in the ion mobility spectrum was composed of two different species. The SU ions responsible for the third peak in the spectrum, labeled c and d, correspond to the protonated primisulfuron-methyl ion (m/z 469) and the sodiated metsulfuron ion (m/z 404), respectively. Figure 7 illustrates the necessity of the QMS as a detection system to identify all ions that contribute to the ion mobility spectrum for certain SU mixtures. However, conclusive mass identification is not necessary for identification of species within all SU herbicide mixtures.

The spectrum in Fig. 8 demonstrates the capacity of the system to separate and identify three SU species within a mixture without the aid of mass identification. The spectra in this figure illustrate the ion mobility separation scheme of sulfometuron-methyl, tribenuron-methyl, and prosulfuron. Given low ion transmission and duty cycle of the instrument, the resolution of the QMS must be reduced to allow an increased number of ions to be detected.

FIG. 8. The spectra in this figure illustrate the ion mobility separation scheme of sulfometuron-methyl, tribenuron-methyl, and prosulfuron. Given low rates of ion transmission, the resolution of the QMS was decreased to allow a larger population of ions to be detected. The sodiated tribenuron-methyl and prosulfuron species have similar m/z values making resolution in the mass dimension difficult with this instrument. However, each species is conclusively identified within the ion mobility spectrum: (a) the SIM ion mobility spectrum of the protonated sulfometuron species and (b) the SIM of the sodiated tribenuron ion and the protonated prosulfuron ion.
In some cases, such as in Fig. 8, species that are unresolved in the mass dimension can be identified conclusively in the ion mobility spectrum. Figure 8a is the SIM ion mobility spectrum of the protonated sulfometuron-methyl species (m/z 365), while Fig. 8b illustrates the SIM of the sodiated tribenuron ion (m/z 418) and the protonated prosulfuron ion (m/z 420). When operating the QMS at a decreased resolution, the two ions differing by 2 amu, as shown in Fig. 8b, are indistinguishable in the mass dimension. However, the mobilities of these two ions are sufficiently different to be

FIG. 9. This series of spectra represent the AP-IM-QMS analysis of an unfiltered Palouse River water sample spiked with 25 ppm sulfometuron-methyl. The blank and the spiked mass spectra differ only by the presence of the 365 [M + H]^+ sulfometuron-methyl ion. The low mass ions (<m/z 120) correspond to the water and solvent clusters formed when using ESI. The lower spectrum illustrates the SIM ion mobility spectrum of the 365 ion.
resolved using high resolution AP-IMS. Given the complexity of SU ion formation using ESI, complicated mixtures of SU herbicides proved difficult to examine without the aid of mass identification. However, a well-characterized mixture of SU herbicides is well within the realm of analysis using IMS.

Environmental Applications

To demonstrate the use of AP-IMS as a rapid environmental screening technique, an unfiltered Palouse River water sample spiked with 25 ppm sulfometuron-methyl was analyzed using the techniques described previously. The status of the water sample used did not warrant filtration; however, under normal circumstances filtration would be necessary to remove any large particulate matter. Figure 9 shows the mass spectrum of the spiked sample in addition to the ion mobility spectrum of the ion. The peaks contained in the lower mass region (<120 m/z) correspond to water and solvent clusters formed using ESI. The inset spectrum shows the blank of the river water. The SIM ion mobility spectrum of the spiked sample revealed a single peak demonstrating the capability of the system to identify individual SU species within an environmental matrix.

Sensitivity Studies

As SU herbicides form a wide range of ions and exhibit various levels of response, quantification of an SU species within a mixture proved extremely difficult. The sensitivity of standard solutions indicated that the instrumental detection limit for SU herbicides ranged from 850 ppb to 5 ppm. Consistently forming a singular [M + H]⁺ ion, sulfometuron-methyl demonstrated the highest degree of response in the AP-IMS-QMS system. Prosulfuron, on the other hand, exhibited the lowest degree of sensitivity despite the formation of only one peak through the ionization process. This characteristic is believed to be due to ionization characteristics of the molecule brought about by the electron-withdrawing fluorine functional groups.

Summary and Conclusions

The successful separation of SU herbicides demonstrated the capability of this system to isolate and detect individual SU ions. This method of SU herbicide analysis represents an alternative to traditional methods of analysis that satisfies the need for a fast and efficient screening method with strong potential for field applications. The two-dimensional high resolution capability of ESI–AP-IMS–MS allowed for ions of similar collisional cross sections and m/z values to be separated. Traditional methods of SU analysis are capable of analyzing low ppb levels. This, however, is possible only after significant sample concentration. This study indicated that the instrumental LOD for SU herbicides using ESI-IMS-MS without sample concentration was in the high ppb range. Concentration of actual samples following extraction would allow for the method detection limit using AP-IMS to directly compete with traditional methods of SU analysis. An added benefit of ESI–AP-IMS aside from the ability to analyze aqueous samples with minimal preparation is the comparatively short data acquisition times. Traditional methods of analysis (LC–MS) acquire data on the minute timescale, whereas this method of SU herbicide analysis using ESI–AP-IMS–QMS required only milliseconds to obtain results. These comparatively rapid analyte separation times combined with the ability of AP-IMS to operate under a wide range of environmental conditions with minimal sample preparation make ESI–AP-IMS an ideal candidate for analysis of aqueous field samples.

References