Coronaspray Nebulization and Ionization of Liquid Samples for Ion Mobility Spectrometry

Christopher B. Shumate and Herbert H. Hill, Jr.*

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

Ion mobility spectrometry after electrospray nebulization and ionization was investigated as a method for the detection of components dissolved in liquids. While electrosprary operating conditions proved promising, greater sensitivity was achieved when the electric potential applied to the sample introduction needle was increased above breakdown potential and a corona discharge was established. Passing the liquid through the corona discharge established a "coronaspray" that efficiently nebulized and ionized the solvent and analytes. In this initial investigation of coronaspray ion mobility spectrometry (CIMS), ion current as a function of potential, temperature, and liquid flow rate was studied; several IMS spectra were obtained; and a continuous monitoring mode of operation was demonstrated. The results from this study indicated that CIMS has potential as a versatile and sensitive detection method for a variety of analytical procedures involving liquid flowing streams such as flow injection analysis, liquid chromatography, capillary zone electrophoresis, and field flow fractionation.

INTRODUCTION

Ion mobility spectrometry (IMS) is an ambient pressure ion separation technique that has been explored as a gas phase analytical monitoring and detection device for trace quantities of organic compounds. Separating ions according to their individual velocities as they drift through an inert gas in an electric field, IMS has been employed as a dedicated trace gas monitor (*1*) and as a versatile detector for gas and supercritical fluid chromatography (*2, 3*). For these applications the analyte was introduced as a neutral vapor and then ionized in the spectrometer by using a radioactive source. Several nonradioactive sources have also been investigated for IMS. Multiphoton ionization demonstrated the selective ionization properties of lasers (*4*) while the practical advantages of direct photoionization were demonstrated for IMS as a chromatographic detector (*5*).

The concept of using electrified liquids to spray ions and obtain mobility spectra can be traced back to Chapman in 1937 when he used an Erikson mobility tube to measure the gas-phase mobility of charged carriers in a variety of liquids that had been electrified from spraying (*6*). Dole et al. obtained the first ion mobility spectrum for an organic compound with electrospray (*7*), followed by unsuccessful attempts to separate oligomers of electrosprayed polystyrene and poly(vinylpyrolidine) (*8*). Although this approach had originally shown promise for high molecular weight determinations, it failed for a combination of reasons. The primary reason for failure was that ion mobility spectrometry did not have sufficient resolution to separate oligomers of polymers or individual components of complex mixtures. Thus, individual oligomers or compounds must be introduced into the electrospray after separation of the polymer or mixture. Even when pure compounds such as lysozyme in ethanol were introduced, peaks were so broad that it was difficult to achieve an accurate mobility value.

The low IMS resolution of early electrospray work can be attributed to three effects. First, the low sensitivity of the electrospray source required the introduction of large quantities of compounds. These amounts could not be efficiently eliminated from the drift tube of the spectrometer and participated in ion–molecule reactions in the ion drift region. Second, liquid flow rates were so large and heat transfer from the carrier gas to the electrosprayed droplets so low that complete evaporation of the solvent had not been achieved prior to entering the ion drift region. Solvent evaporation from the ion droplets in the drift regions caused band broadening of the ion peak. A third contribution to low IMS resolution may have been drift field perturbation from the electrical potential of the electrospray needle. Thus, problems associated with electrospray ion mobility spectrometry appeared to be too difficult for the technique to be of practical significance. After a number of years of investigation of electrospray ion mobility spectrometry, Gieniec et al. concluded that electrospray would turn out to be useful when the ions could be analyzed in a mass spectrometer rather than an ion mobility spectrometer (*9*).

Nevertheless, we believed that the electrified spray process still provided considerable potential for ion mobility spectrometry, especially when applied as a detector for liquid chromatography and related analytical methods. Initial investigations by this laboratory attempted to solve the problems associated with the electrospray process by using a unidirectional flow ion mobility spectrometer (*10, 11*). Results from these investigations proved to be extremely encouraging and it appeared that the unidirectional flow approach effectively swept the neutrals from the drift region while more efficiently evaporating the solvent from the charged droplets.

During the course of these investigations it became apparent that conditions other than those employed for electrospray may be beneficial for the nebulization and ionization of liquids into the ion mobility spectrometer. The purpose of this paper, therefore, is to present some of our initial investigations on electrospray ion mobility spectrometry and to report on the potential of an alternative, although related, method which we call coronaspray ion mobility spectrometry (CIMS).

EXPERIMENTAL SECTION

Initial Investigations. Initial investigations were performed with an IMS nebulization/ionization observation prototype in which a glass tube was substituted for the ion drift tube. A schematic of the prototype is shown in Figure 1. It was a simple design consisting of a stainless steel repeller plate, a coronaspray needle, a reference ring, a drift ring, and a collector electrode assembly. The drift ring and collector electrode were taken directly from one of our existing ion mobility spectrometers. A glass tube was mounted on top of the drift ring to serve as support for the repeller plate, through which the sample was introduced via a 100 μm i.d. fused silica capillary. Inside the prototype, the fused silica capillary was butt-connected to a 33-gauge stainless steel needle that was connected to the high voltage directly through the glass tube. The needle and the repeller plate were insulated from each other by the polyimide butt-connected ferrule.

Electrical potential for the entire prototype was provided by a single 5000-V high-voltage supply (Model PMT 50A, Bertan

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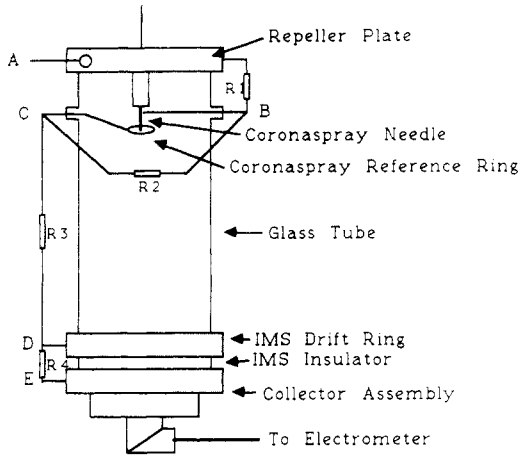

Figure 1. Electrospray prototype: corona ring, 1 cm diameter; R1, R2, R3, and R4 represent resistors at values of 1.25 MΩ, 2.5 MΩ, 6.2 MΩ, and 50 kΩ, respectively. Conditions to initiate spray were (A) 4000 V, (B) 3500 V, (C) 2500 V, (D) 20, and (E) ground. Typical total ion current was 7 nA.

Assoc., Hicksville, NY). This was the same supply that was typically used to generate the field in our standard ^{63}Ni source ion mobility spectrometers; thus the total potential available for the experiment was 5 kV. Moreover, since only one voltage supply was available, all potentials had to be referenced to this supply. Thus the repeller plate, coronaspray needle, coronaspray reference ring, IMS drift ring, and collector electrode were connected in series with the power supply by using appropriate resistors to set the desired relative potentials among these components. Typical resistor values for R1, R2, R3, and R4 shown in Figure 1 were 1.25 MΩ, 2.5 MΩ, 6.3 MΩ, and 50 kΩ, respectively. Thus, in order to change the potential on the needle, the potentials on all other components of the system were affected.

The prototype was housed in a converted laboratory drying oven which provided a stable temperature of 150 °C for the experiments. Sufficient oven volume facilitated construction and modification of the prototype, and a glass door permitted observation of the spray process during operation. This oven was the same as that used in the development of unidirectional flow ion mobility spectrometry in our laboratory in 1982 (*2*).

Sample liquids were introduced into the prototype at flow rates from 5 to 100 μL/min by using a low flow syringe pump (Brownlee MPLC Micropump, Brownlee Labs Inc., Santa Clara, CA).

Coronaspray Ion Mobility Spectrometer. Once the initial experiments with the prototype were complete, a unidirectional flow, two gate, ion mobility spectrometer was constructed similar to one described earlier (*3*), except that the ^{63}Ni ionization source was removed and replaced with a coronaspray needle, which served as the introduction port for liquid samples.

Figure 2 is a schematic of the coronaspray ion mobility spectrometer used in work presented in this paper. The spectrometer was mounted in a vertical position with the collector assembly at the bottom and the coronaspray needle at the top. This positioning was, however, only one of convenience and it would be possible to invert or horizontally mount the spectrometer directly onto an analytical separation device such as a liquid chromatograph. In this configuration, a capillary fused silica transfer line entered the spectrometer at the top (A) and transferred the flowing liquid sample to a stainless steel coronaspray needle which was 2 cm in length and 33 gauge. The position of the needle in the spectrometer could be adjusted by changing the needle length or by the addition or deletion of ion mobility drift rings (F) prior to the ion entrance gate (H).

The source block (D) was held in place with a glass insulating sleeve (B) and was fabricated from Teflon, providing excellent isolation for the high voltage connection (E) but limiting the operating temperature to less than 225 °C. A gas exit port (C) was drilled through the Teflon to permit the drift gas and solvent vapors to be swept efficiently from the spectrometer. In this design, the entire length of the spectrometer was purged continuously by either nitrogen or air that was introduced (K) below the collector screen (J). This unidirectional flow design was first

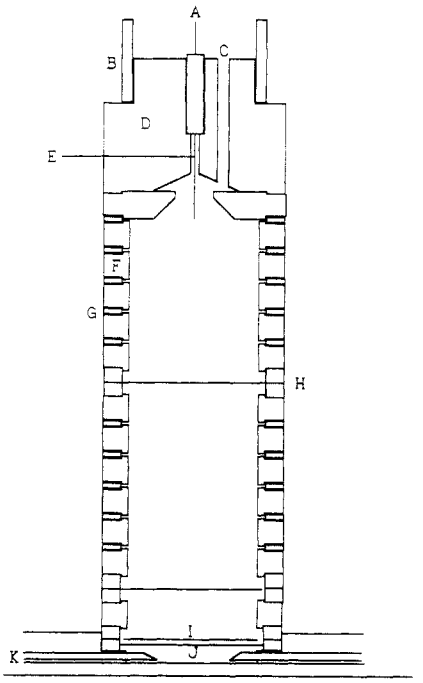

Figure 2. Schematic of ion mobility tube: A, fused silica liquid transfer line; B, glass insulating sleeve; C, gas exit port; D, Teflon source block; E, electrical connection; F, stainless steel voltage rings; G, Teflon insulator rings; H, ion entrance gate; I, aperture grid; J, ion collector screen; K, drift gas entrance.

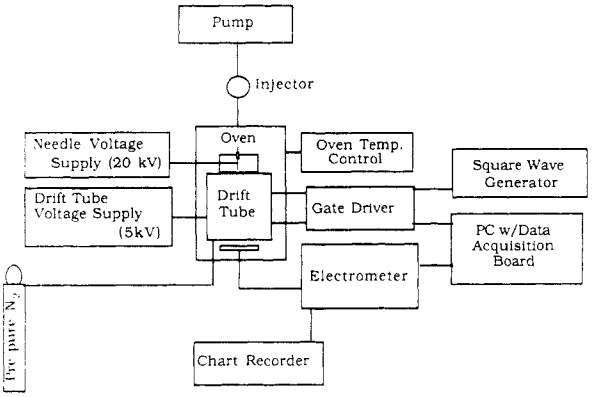

Figure 3. Block diagram of coronaspray ion mobility spectrometer. Two-voltage supply system, used for Figures 7–9.

introduced for ion mobility spectrometers in 1982 (*2*) and appears to be an effective method for keeping the drift region of an ion mobility spectrometer free from residual sample.

The ion mobility drift tube was similar to other tubes constructed in this laboratory in which an alternate series of stainless steel voltage rings (F) and Teflon insulator rings (G) were stacked to form a 14 cm long closed tube. A resistor chain consisting of 12 matched 1-MΩ resistors connected the stainless steel voltage rings to drop the voltage evenly over the distance of the tube, creating a uniform electric field of about 250 V/cm through which the coronaspray-produced ions drifted.

The ion drift tube was segmented by the two ion gates (H) into three regions. The first region, between the needle and the ion entrance gate, was called the evaporation region. Here, heat transfer from the drift gas served to evaporate the solvent from the electrified droplets until, ideally, they reached a stable mass. The second region, between the ion entrance gate and the ion exit gate, was the ion drift region. It was between these two gates that the drift times of the ions were measured. The last region, between the exit gate and the collector, was the collection region. Here it was important to collect the ions as rapidly and efficiently as possible.

Figure 3 provides a block diagram showing the specific components of the entire spectrometer. The dual piston syringe pump

(MPLC micropump, Brownlee Labs, Inc., Santa Clara, CA) was capable of delivering stable flows down to 1 μL/min. The injector was a four-port, 60-nL internal volume injector (Valco C14W, Valco Industries, Houston, TX). Two separate voltage supplies were used so that the drift voltage and the needle voltage could be set independently. The needle voltage supply was a 20-kV supply (Bertan 602B-200, Bertan Associates, Hicksville, NY) and the drift tube supply was a 5-kV supply (Bertan PMT-50A, Bertan). The drift gas used for these experiments in which only positive ions were investigated was prepure nitrogen (Liquid Air Corp., San Francisco, CA). The electrometer was a Keithley 427 (Keithley Instruments, Inc., Cleveland, OH) and the chart recorder was an OmniScribe (Houston Instruments, Austin, TX). The drift tube, gate driver, square wave generator, and oven temperature controller were all constructed by the Washington State University Technical Services group.

RESULTS AND DISCUSSION

Initial investigations of the electrospray system involved the IMS prototype shown in Figure 1. The Pyrex tube mounted in the large lab oven permitted the observation of the liquid flowing from the needle. With a liquid flow rate of 5 μL/min and no voltage on the needle, 2-propanol dripped slowly out of the needle and collected in a puddle on the ion collection plate at the bottom of the apparatus. As the voltage was increased a nearly invisible spray occurred when approximately +3500 V (a differential of about +1000 V between the ring and the needle) was applied to the needle. As the voltage was increased further, a corona discharge was observed at the needle. Under these conditions, the maximum current obtained from coronaspray was between 5 and 7 nA measured at the Faraday plate. Solvents investigated for spraying included water, methanol, 2-propanol, acetone, THF, acetonitrile, hexane, and dilute phosphoric and acetic acid. Once we were convinced visually that liquids really could be made to spray and we could identify two regions (corona and pre-corona) under which the spray could be observed, the needle source was removed from the Pyrex tube and adapted to the ion mobility spectrometer described in Figure 2.

Total Ion Current. With both the entrance and the exit gates of the ion mobility spectrometer held open, the total ion current produced as a function of electrical potential applied to the needle was measured for three conditions. In the first case, the needle consisted of a solid metal probe 0.5 mm in diameter and tapered to a point. In the second case, the needle was a 27-gauge hypodermic needle in which no liquid flow was passed. In the third condition, a 5 μL/min flow of methanol was pumped through the 27-gauge needle. The results of these experiments are shown in Figure 4.

When the solid needle was employed, no current could be measured below an applied potential of about 3800 V. Above this voltage more than 0.6 nA of current would be measured in the spectrometer. The cut-off between the condition of current and no current was sharp, indicating the onset or quenching of a discharge. While the exact voltage at which this current/no current boundary occurred depended upon temperature, gas flow rate, and whether the voltage was being increased or decreased, the basic shapes of the data shown in Figure 4 were reproducible. Although we could no longer make a visual inspection of the probe, the current–voltage (*IV*) behavior suggested that a corona discharge was occurring at the needle tip when the voltage was greater than 3800 V, creating charge carriers from the breakdown of the nitrogen gas.

When the solid needle was replaced with a 27-gauge hypodermic needle, a similar behavior to the *IV* characteristics was observed although the current at a given voltage was greater for the capillary tube than for the solid needle and the current cut-off occurred at a lower voltage. Presumably, these differences in the *IV* characteristics of the two probes

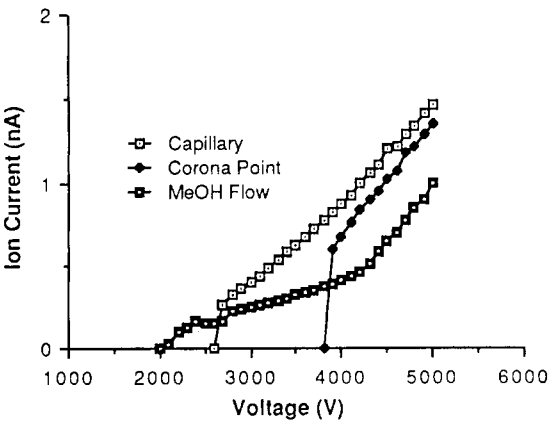

Figure 4. Total ion current as a function of needle voltage. "Capillary" represents the condition in which there was no liquid flow through the needle. "Corona point" refers to a solid needle in place of the capillary needle. "MeOH flow" indicates a methanol flow of 5 μL/min through the capillary coronaspray needle. Conditions were as follows: needle voltage, varied from 2000 to 5000 V; drift field, varied from 100 to 250 V/cm; temperature, 150 °C; pressure, 702 Torr; positive mode; nitrogen drift gas, 600 mL/min.

were due to shape and surface area at the probe tip. The *IV* characteristics however were indicative of the corona discharge condition.

When 5 μL/min of methanol was introduced into the spectrometer through the capillary, ion current was significantly decreased with respect to that which was obtained when no liquid flowed through the tube. For example, with 3500 V on the capillary tube and 5 μL/min of methanol flowing through the tube, 0.2 nA of current was obtained. When no methanol flowed through the tube, 0.6 nA of current was observed for the same applied potential. More importantly, when the voltage was decreased below the current cut-off position, ion current could still be measured when 5 μL/min of methanol was passing through the capillary.

In Figure 4, the corona cut-off potential occurred at about 2700 V on the capillary. When flow was passing through the capillary, current could still be observed below this voltage and decreased incrementally as the voltage was decreased down to 2000 V. Below 2000 V no current could be observed either with or without flow through the capillary.

While it has been shown by mass spectrometry that the ions produced with electrospray and corona discharge are different (*13*), the gain in signal that was obtained by operating in the corona discharge region warranted further investigation of this region as a nebulizer/ion source for IMS. For the purposes of this paper, we define coronaspray as the nebulization/ionization process that occurs when a liquid is passed through a capillary tube in which the applied potential is greater than the corona cut-off potential. Electrospray, as always, refers to the nebulization/ionization process that occurs when the applied potential is below the corona cut-off potential. The remainder of this study focuses on the characterization of the coronaspray conditions for nebulization and ionization in the IMS.

Total ion current also depended on the liquid flow rate and the temperature of the spectrometer. Figure 5 shows the results of an investigation in which the methanol flow rate was varied from 5 to 45 μL/min and the operating temperature of the spectrometer was varied from 20 to 200 °C. Current increased as a function of increasing temperature and decreasing flow rate. A maximum current of 1.6 nA was achieved under these conditions when 5 μL/min of methanol was pumped through the needle at 200 °C.

Ion Mobility Spectra. Figure 6 shows the first ion mobility spectrum taken with the unidirectional flow ion mobility spectrometer with coronaspray nebulization and ionzation.

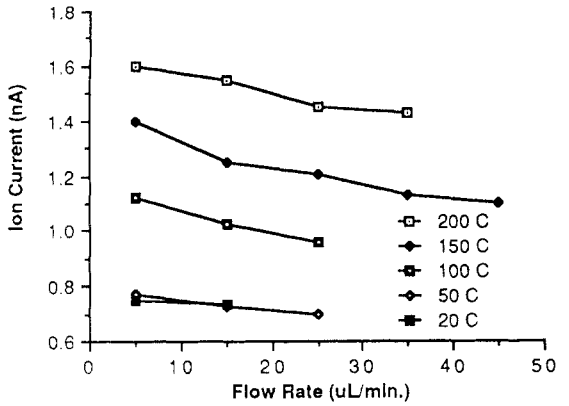

Figure 5. Ion current as a function of methanol flow rate and temperature: needle voltage, 5000 V; drift field, 250 V/cm; nitrogen drift gas, 600 mL/min; both ion gates open; pressure, 699 Torr.

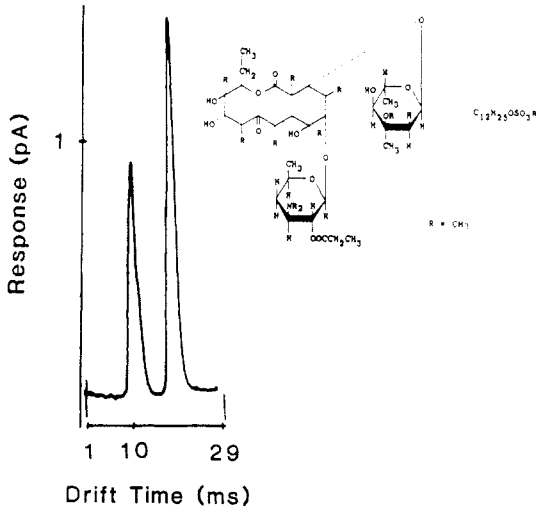

Figure 6. Scanning second gate spectrum of erythromycin estolate: total scan time, 3.0 min; methanol flow rate, 5 μL/min; drift field, 250 V/cm; coronaspray needle voltage, 5000 V; nitrogen drift gas flow rate, 600 mL/min; temperature, 150 °C; pressure, 690 Torr.

The spectrum shown is of erythromycin estolate which has a molecular weight of 1056 amu. This compound is too large and too polar to be introduced into the ion mobility spectrometer by volatilization methods. Introduction of the compound was via a liquid stream of methanol at a flow rate of 5 μL/min. A concentration of 5 mg/mL was continuously pumped into the spectrometer. The spectrum was obtained by operating the spectrometer in a mode know as the scanning second gate (SSG) method. In this mode, the entrance ion gate was pulsed open for 0.2 ms and the exit ion gate was pulsed open at some delay time after the entrance gate pulse. At a preselected cycle time of 30 ms, the process was repeated with the exit gate pulse coming slightly longer than in the last cycle. Thus by this "box car integration" method, an entire spectrum could be obtained. For the spectrum shown in Figure 6, 3 min of collection time was required. Although the SSG method was slow, the data obtained were extremely promising. Good resolution between the solvent peak, methanol, and the analyte peak, erythromycin estolate, demonstrated that nonvolatile compounds could produce clean ion mobility spectra. The peak that occurred at about 10 ms was due to the methanol and was always present as background even when no erythromycin estolate was introduced into the spectrometer. When erythromycin estolate was introduced, a peak at about 20 ms would appear while the intensity of the peak at 10 ms would decrease. In general, work with the SSG mode of the spectrometer indicated that ion mobility was possible with coronaspray and that the data were

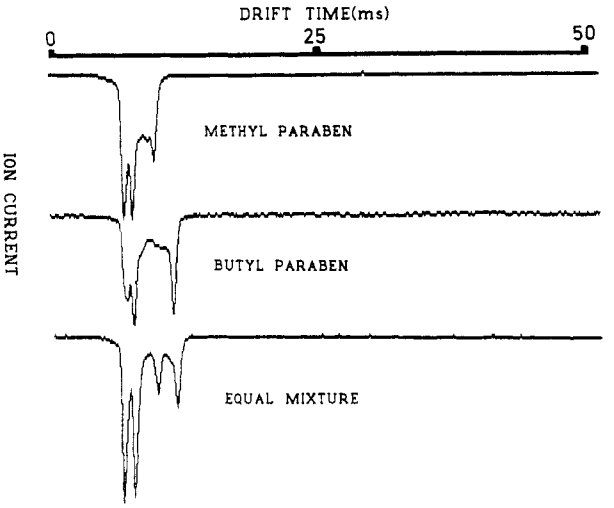

Figure 7. Signal averaged spectra of methyl and butyl paraben: total scan time, 0.2 s; methanol/water flow rate, 10 μL/min; drift field, 250 V/cm; needle voltage, 6500 V; nitrogen drift gas, 700 mL/min; pressure, 695 Torr; temperature, 184 °C.

similar to that obtained after gas or supercritical fluid introduction.

Encouraged by the positive results of the SSG mode of operation, a faster method for obtaining spectra was employed that enabled more rapid collection of data. By use of a signal averaged (SA) method several scans of the entire spectrum were averaged to obtain the spectra shown in Figure 7. With this method the entrance gate was pulsed open for a few tenths of a millisecond while the exit gate was held open during the entire collection process.

The solvent of Figure 7 was a binary system of methanol/water. Two peaks for the solvents can be seen in the early portion of the spectra. With the SA mode, data collection was fast enough to make discrete injections of the samples into a flowing stream and capture the spectra as the compounds passed through the spectrometer.

As can be seen from the figure, both methyl paraben and butyl paraben were separated from the solvent ions. In the top spectrum the first peak was presumably due to water, the second peak to methanol, and the third peak to methyl paraben. In the middle spectrum, the first two peaks were due to the water and methanol and the third peak was due to butyl paraben. The bottom tracing shows a spectrum that resulted from the introduction of an equal mixture of methyl and butyl paraben. While this laboratory has emphatically maintained that ion mobility spectrometry should not be viewed as a separation/identification method and should primarily be used after high-quality separation procedures, the separation of these two product ions demonstrated that for certain well-defined systems, CIMS may have potential for the analysis of liquid mixtures. Thus, CIMS may be important as a detection method for flow injection analysis (FIA) techniques.

Figure 8 shows yet a third method for obtaining ion mobility spectra. Developed in this laboratory several years ago (*12*), the Fourier transform (FT) mode of operation has the advantage of rapid scanning without requiring a high-speed electrometer. These spectra demonstrated the response of organic acids with coronaspray ionization. In the top tracing, the first peak was presumably due to water, the second peak to methanol, and the third peak to the analyte acetylsalicyclic acid. The middle tracing showed responses from the same solvent system along with an ion peak from sulfanilic acid. Finally, the lower tracing demonstrated the response of trichlorophenoxyacetic acid in pure methanol.

Continuous Mobility Monitoring. As a detection method

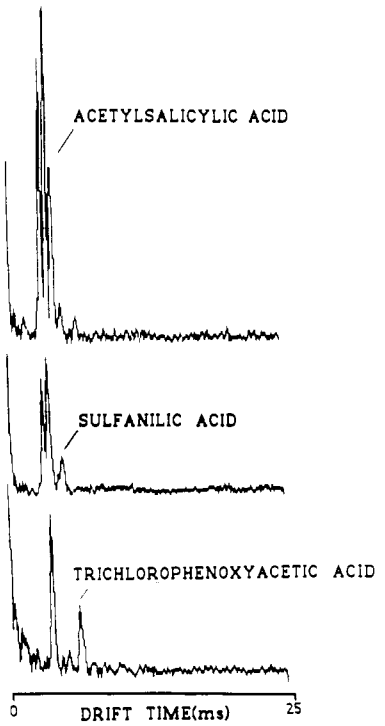

Figure 8. Fourier transform spectra of organic acids: total scan time, 4 s, methanol flow rate, 5 μL/min; drift field, 320 V/cm; needle voltage, −8000 V; air drift gas, 800 mL/min; pressure, 697 Torr; temperature, 152 °C.

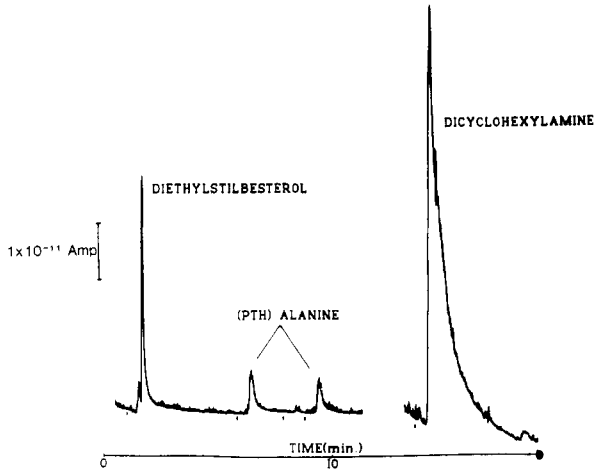

Figure 9. Continuous monitoring mode: 50 ng of diethylstilbesterol, 50 ng of phenylthiohydantoin–alanine, and 60 ng of dicyclohexylamine; chart speed, 1 cm/min; methanol flow rate, 5 μL/min; needle voltage, +7100 V; temperature, 184 °C; drift time window, 8–48 ms; nitrogen drift gas, 800 mL/min; drift field, 310 V/cm; pressure, 694 Torr.

for liquid separation processes, the coronaspray ion mobility spectrometer would be operated in the continuous mobility monitoring mode. That is, a preselected window of drift time would be continuously monitored for a change in intensity. The window could be chosen to correspond to the drift time of the solvent ions that would decrease in intensity as analytes passed through the spectrometer or they could be chosen to monitor drift times that corresponded to drift times of ions created from the compounds of interest. Although the window size may be narrowed to gain response selectivity, a wide window was chosen for conditions under which Figure 9 was obtained. For these experiments, the drift time window excluded ions produced from the solvent but monitored all drift times longer than those of the solvent ions.

Continuous mobility monitoring responses that were created by discrete injections of diethylstilbesterol, PTH-alanine, and dicyclohexylamine are shown in Figure 9. Points of injection are denoted on the tracing by small "tick" marks located just below the base line. The compounds shown here provided good sensitivity and reproducibility from injection to injection. PTH-alanine is shown twice in this figure with a blank injection in between, demonstrating, in a qualitative way, typical short-term reproducibility of the detector. Quantitative investigations of long-term detector reproducibility have not yet been completed.

Table I. Compounds That Provided CIMS Spectra

triisopropanolamine	lysine
tri-*n*-butylamine	glycine
dibenzylamine	methionine
diphenylamine	asparagine
caffeine	alanine
indole	phenylethylamine
chloropropionic acid	acetylsalicyclic acid
Aroclor 1242 (PCB)	ascorbic acid
trichlorobenzene	sulfanilic acid
trichloroacetic acid	trichloropropionic acid
trichlorophenoxyacetic acid	
trinitrotoluene	
erythromycin estolate	lutidine
methylparaben	butylparaben
phenylbutazone	Tris (THAM)
o-cresol	tricresol phosphate

Qualitative Survey of Compounds. Extensive quantitative investigations of response factors have not yet been attempted, although a qualitative survey of a rather limited number of compounds has been completed. Table I provides a list of compounds that have provided spectra and show potential for detection by CIMS. It is expected, however, that a wide variety of compounds will respond in CIMS in a sensitive manner.

The response of high molecular weight compounds, underivatized polar compounds, compounds that are not electroactive, and compounds that do not absorb ultraviolet radiation has been observed. Certainly there remain many unanswered questions. What is the long-term reproducibility? Does ion fragmentation occur? What are the optimal parameters? How low can the noise level be? How many more solvents are compatible with the method? How universal is the detector?, etc. Nevertheless, these initial investigations of coronaspray ion mobility spectrometry have demonstrated a strong potential for the development of this method as an analytical tool for the detection of compounds in liquid samples. As a detection method for microbore liquid chromatography, capillary zone electrophoresis, flow injection analysis, field flow fractionation, and other liquid-based analytical methods, coronaspray or electrospray ion mobility spectrometry appears to offer an exciting potential for nonvolatile and high molecular weight compounds.

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Noise Power Spectral Characteristics of an Inductively Coupled Plasma Mass Spectrometer

Jeffrey S. Crain, R. S. Houk,* and David E. Eckels

Ames Laboratory—U.S. Department of Energy and Department of Chemistry, Iowa State University, Ames, Iowa 50011

The noise power spectra of $^{85}Rb^+$ signal and $^{93}Nb^+$ signal from an inductively coupled plasma mass spectrometer were measured at the same plasma conditions as were those of Sr II emission from the plasma itself. Comparison of these spectra showed that discrete frequency noise in the emission at the mass spectrometer sampling orifice is nearly identical with that in the mass spectrometric signal and that white noise in the mass spectrometer signal was higher than that found in the emission signal. The dependence of noise frequencies on plasma operating conditions was generally the same for both measurements and was generally the same as that expected of emission from the plasma alone, i.e., when the plasma was not being sampled for mass spectrometry. However, discrete frequency noise in emission from the plasma alone differed substantially in frequency from that in the mass spectrometric signal. These results indicate that the plasma is the source of discrete frequency noise in the mass spectrometric signal and that the discrete noise frequencies can be affected by changes in plasma gas dynamics due to interaction between the plasma and the mass spectrometer sampling interface. The major source of signal instability in this particular inductively coupled plasma mass spectrometer was found to be 1/f noise.

INTRODUCTION

Since the advent of inductively coupled plasma mass spectrometry (ICP-MS) in the late 1970s, investigators have found many valuable applications of this technique. Among these applications are trace elemental and isotopic analysis of geological materials (*1–5*), stable isotope tracing of metabolic pathways in living organisms (*6*, *7*), and trace elemental analysis by isotope dilution (*8–10*). However, there is general agreement that the precision achievable by ICP-MS stands in need of improvement. For example, isotope ratios measured by ICP-MS have relative standard deviations (RSDs) ranging between 0.3% and 1.0% for commercially available instruments. However, the exceptional precision of thermal ionization mass spectrometry (typically 0.01% RSD) makes it the technique of choice when small isotope ratios or small isotope enrichments are to be measured and when sample throughput is not a consideration. Houk and Thompson (*11*) have discussed the factors limiting the precision of ICP-MS isotope ratios and, based upon the findings of other workers (*6–8*, *12–14*), have concluded that the precision of isotope ratios measured by ICP-MS is primarily limited by instrumental stability. Currently, the signal stability of commercially available ICP mass spectrometers is around 5% RSD over a period of several hours. A logical step in the advancement of ICP-MS as a technique for elemental and isotopic analysis is to improve these figures for stability and precision. Therefore, the sources of instrumental noise in an ICP mass spectrometer should be isolated and characterized, such that the deleterious effects of instrumental noise on measurement precision can be minimized.

To date, no studies of ICP-MS noise power spectral characteristics have appeared in the literature. However, a number of investigators have reported studies of noise power for the ICP as an optical emission source (*15–19*). These studies have found that, in general, the noise power spectral characteristics of ICP emission depend on plasma operating parameters and torch design. Belchamber and Horlick (*16*) showed that discrete frequency noise in ICP emission could be attributed to the rotation of an asymmetric plasma, but Winge et al. (*19*) have proposed an alternate mechanism for discrete frequency noise production involving the vortex ring phenomenon (*20*). In the present work, no attempt is made to elucidate the mechanisms by which noise is produced in the ICP mass spectrometer. However, comparisons between mass spectral noise and optical noise from both the emission of the ICP alone and emission of the ICP during sampling for mass spectrometry are made, and preliminary connections are drawn between the three.

EXPERIMENTAL SECTION

The ICP mass spectrometer used in this study has been described previously (*21*). The detector assembly used in these experiments was modified from that described above. In this new assembly, the scintillator detector was replaced by an channeltron electron multiplier offset 90° from the center line of the quadrupole mass analyzer. An ion deflecting plate, aligned with the mouth of the channeltron, was placed immediately below the cylindrical exit lens of the mass analyzer such that ions exiting the quadrupole were steered toward the entrance aperture in the detector housing. The voltages applied to these ion optical elements are given in Table I. A detector assembly having similar geometry and components has been described previously (*25*).

The operating conditions and components of this instrument are described in Table I. A schematic diagram of the experimental apparatus is shown in Figure 1. In the mass spectrometric experiments, ion signals for $^{85}Rb^+$ and $^{93}Nb^+$ were measured by nebulizing a solution of Rb and Nb, each at 1 mg L^{-1}. The kinetic

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