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Electrospray Ionization High-Resolution Ion Mobility Spectrometry for the Detection of Organic Compounds, 1. Amino Acids

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Our aim in this investigation was to demonstrate the potential of the high-resolution electrospray ionization ion mobility spectrometry (ESI-IMS) technique as an analytical separation tool in analyzing biomolecular mixtures to pursue astrobiological objectives of searching for the chemical signatures of life during an in-situ exploration of solar system bodies. Because amino acids represent the basic building blocks of life, we used common amino acids to conduct the first part of our investigation, which is being reported here, to demonstrate the feasibility of using the ESI-IMS technique for detection of the chemical signatures of life. The ion mobilities of common amino acids were determined by electrospray ionization ion mobility spectrometry using three different drift gases (N_2, Ar, and CO_2). We demonstrated that the selectivity can be vastly improved in ion mobility spectroscopy (IMS) in detecting organic molecules by using different drift gases. When a judicial choice of drift gas is made, a vastly improved separation of two different amino acid ions resulted. It was found that each of the studied amino acids could be uniquely identified from the others, with the exception of alanine and glycine, which were never separable by more then 0.1 ms. This unique identification is a result of the different polarizabilities of the various drift gases. In addition, a better separation was achieved by changing the drift voltage in successive experimental runs without significantly degrading the resolution. We also report the result of our analysis of liquid samples containing mixtures of amino acids.

Strategies are being developed by the major space agencies (i.e., NASA, the European Space Agency, etc.) to pursue astrobiological objectives for in-situ exploration, such as determining the abundance and distribution of biogenic elements and organic compounds, detecting evidence of ancient biota on these bodies, and determining whether indigenous organisms exist anywhere on Mars, Europa, and Titan. Biosignatures of past life may still exist today on both Mars and Europa in some protected subsurface environments, such as beneath the surface of Martian polar ice caps[1] or inside the icy surface of Europa.[2] State-of-the-art detection techniques that would be highly selective and sensitive (part per billion) to specific organic compounds, which are also suitable for in situ detection of large organic molecules of biological importance, will play a major role in these endeavors.

Ion mobility spectrometry (IMS) has many features that make it attractive as an analytical separation device. IMS is simple, fast, rugged, highly selective, and very sensitive to a wide range of compounds. IMS is a sensitive detection technique, because one can readily measure ion currents below 10^{-12} amps.[3] Because of the above, IMS has found wide use for the detection of volatile chemical compounds such as explosives, narcotics, and chemical warfare agents.[4] As a result of the recent developments in electrospray ionization (ESI) technique, investigators have been able to carry out analyses of nonvolatile chemicals directly from liquid-phase samples utilizing IMS in tandem with ESI.[5] The development of ESI-IMS greatly expanded the range of compounds to include nonvolatile samples dissolved in a liquid sample that could be analyzed by IMS. However, the employment of the technique for liquid mixtures was still somewhat limited by the lack of sufficient resolving power.[6] More recently, ambient-pressure high-resolution IMS systems have been developed,[7,8,9] which allows the technique to be used as a stand-alone separation device. Recently, the IMS technique has been utilized successfully for the analysis of biomolecular mixtures in an ESI-ion trap/IMS/time-of-flight mass spectrometry analysis of protein/peptide mixtures.[10]

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The fundamentals and applications of the IMS technique are reviewed in detail elsewhere.[4] In brief, the operation of an IMS analyzer is similar to that of a time-of-flight mass spectrometer, except that it can function at atmospheric pressure. When an ion at a given pressure is placed in a constant electric field, it migrates along the direction of the field until it collides with a neutral molecule; it then accelerates again until it suffers another collision, and so forth. The energy gained from the electric field is randomized by these collisions, and the combination of acceleration and collision over macroscopic distances results in a constant average ion velocity ($\bar{v}_d$ in the equation below) which is directly proportional to the electric field (E). The ratio of the ion velocity to the magnitude of the electric field is called the ion mobility (K^m), which is usually specified in units of $cm^2\ V^{-1}\ s^{-1}$, and is given by

$$K^m = (\bar{v}_d/E) = (L/t_dE) = (L^2/Vt_d) \quad (1)$$

Here, L is the ion drift distance in cm, V is the voltage drop across L, E is the electric field and t_d is the time required for the ion to traverse L. The separation of ions on the basis of mobility differences is called ion mobility spectrometry. The separation process and selectivity in IMS are a function of both ion size and mass rather than being dependent solely upon the mass, as in mass spectrometry. Mobility differences impart a second dimension of selectivity to IMS analyses, apart from the ionization preferences. In other words, the ion mobilities depend not only on the mass but also on the collisional cross section of the drift gas and, thus, on the shape of the molecule. Furthermore, the mobility of an ion will depend on the neutral gas number/density and temperature. The dependence of the number density is removed by reporting the ion mobility, K^m, at temperature and pressure conditions corresponding to 273 K and 760 torr, respectively. Thus, the results are reported in terms of the reduced mobility K_0^m in order to remove the dependence upon ambient conditions[8] and follow the relation

$$K_0^m = K^m(273/T)(P/760) = (L/t_dE)(273/T)(P/760) \quad (2)$$

where T is the temperature (K) and P is the pressure (Torr).

The use of different drift gases alters the separation factor (α) in the IMS spectra and, thus, affects the separation selectivity.[11] The separation factor α is defined as

$$\alpha = K_{01}/K_{02} \quad (3)$$

where K_{01} is the reduced mobility of the faster compound, and K_{02} is that of the slower compound. By utilizing different drift gases (He, Ar, N_2, and CO_2) a drastically improved separability of several low-weight compounds, including iodoaniline and chloroaniline and three peptides, was achieved.[11]

Because amino acids represent basic building blocks of life, we used common amino acids to conduct the first part of our investigation, which is being reported here, to demonstrate the feasibility of using ESI-IMS technique for the detection of organic compounds. Of note here, feasibility studies of peptides (amino acids compounds) and mononucleotides (a group of molecules that, when linked together, form the building blocks of DNA or RNA) using ESI-IMS technique is being carried out to further demonstrate the potential of this technique, and the results will be reported in the future.

In the present investigation, we have determined the drift times and the reduced mobility constants for 19 common amino acids found in terrestrial biology using N_2, Ar, and CO_2 as drift gases. Of note here, the 20th common amino acid, cysteine, was not included in the present investigation, because it does not readily dissolve in the solvent that was employed. We demonstrated that the selectivity could be vastly improved in IMS by using different drift gases. We also report the result of our analysis of liquid samples containing mixtures of amino acids and demonstrate the potential of the high-resolution ESI-IMS technique as an analytical separation tool in analyzing biomolecular mixtures to pursue astrobiological objectives of searching chemical signatures of life for in-situ exploration of solar system bodies.

EXPERIMENTAL APPARATUS

All 19 common amino acids that were studied in this investigation were purchased from Sigma Chemical Company (St. Louis, MO) and used without further purification. All solvents (water, acetic acid, and methanol) were HPLC grade and were purchased from J. T. Baker (Phillipsburgh, NJ). Samples were prepared by weighing out known quantities of amino acids and then dissolving them in a solvent solution consisting of 47.5% water, 47.5% methanol, and 5% acetic acid. The sample concentrations were approximately 5 parts per million (ppm). The 19 common amino acids were sprayed into the IMS spectrometer to determine their drift times and ion mobility constants (K_0^m).

The ESI-IMS instruments used in this investigation were constructed at Washington State University (WSU) at Pullman. The details of the ESI unit have been given previously in ref 12. A detailed description and schematics of the high-resolution IMS instrument were also provided in an earlier publication[8] with modifications[6]. In the next few paragraphs, we will briefly summarize the general operating conditions of the ESI-IMS apparatus.

The ion mobility spectrometer was interfaced to a CQ-150 quadrupole mass spectrometer (ABB Extrel; Pittsburgh, PA). The ions entered the mass spectrometer (MS) via a 40-μm aperture and were collected by the electron multiplier located at the back of the MS. The aperture served as the barrier between the atmospheric pressure of the IMS and the vacuum of the mass spectrometer. The ion mobility spectrometer had a drift length of 22.5 cm and was always operated in the positive mode. Different magnitudes of drift voltage were employed for different drift gases. As explained elsewhere,[5] for a given gate width, separation (resolving) power of the IMS instrument changes with the drift voltage applied between two grids. There is a drift voltage that corresponds to a maximum resolving power for a given drift gas. To achieve maximum separation power, we employed the following drift voltages: ~7800 and 6050 V (an electric field strength of 346.9 V/cm and 268.9 V/cm) for N_2, 6400 V (284.4 V/cm) for Ar, and 8700 V (386.7 V/cm) for CO_2.

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Table 1. Typical Operating Conditions during the Experimental Runs

temp (desolvation, drift)	250 °C
drift gas flow rate (N_2, Ar, CO_2)	800 mL/min
cooling gas (N_2 only)	150 mL/min
drift length	22.5 cm
ESI flow rate	5 μL/min
Data Acquisition Parameters:	
no. averages	1000
pulse width	0.2 ms
scan time	50.0 ms
no. points	1000
total spectra time	50 s

The drift tube was held at a constant temperature of 250 °C at the local atmospheric pressure (~700 Torr at Pullman, WA). A counter flow of preheated drift gas (N_2, Ar, and CO_2) was introduced at the end of the drift region at a flow rate of ~800 mL/min.

The sample solution was delivered via an LC pump into a metal spray needle at a flow rate of 5 μL/min. The needle was water-cooled to prevent the heated drift/drying gas from causing solvent evaporation inside the needle. The electrospray was drawn by electric potential into the entrance of the desolvation region (7.2 cm in length) of the spectrometer, where the charged mist migrates in an electric field through a counterflow of heated drift gas. During the few milliseconds of migration through the desolvation region, solvent evaporates from the droplets, and ions are introduced into the drift region of the instrument through an ion gate located at the entrance. Once the gate is "open", the ions are introduced into the drift region, and they accelerate under the influence of an electric field until they pass into the MS region, where they pass through a pinhole and are collected by the electron multiplier on the Extrel quadruple mass spectrometer. Table 1 summarizes the operating conditions under which the IMS spectra were taken.

All mobility data were collected by replacing the stock preamplifier with a Keithley 427 amplifier (Keithley Instruments; Cleveland, OH) and sending the amplified signal to the data acquisition system, again constructed at WSU. A detailed description of the IMS data control and acquisition system was reported previously.[8] All data shown of the individual amino acids were the average of 1000 individual 50 ms spectra, resulting in a total experimental run time of one minute.

RESULTS AND DISCUSSION

Mobility of Ions at Different Drift Voltages and in Different Drift Gases. The spectra in Figure 1 were obtained with N_2 as a drift gas at a concentration of 5 ppm. (Note: the present instrument is capable of detecting amino acids with a sensitivity on the order of 50 parts-per-billion with a good signal-to-noise ratio. However, higher concentrations of amino acids were chosen because of practical considerations.) The spectra of amino acids were clearly visible in each run above residual peaks in the spectra. The residual peaks can, for the most part, be attributed to minor contamination of previously sampled amino acid residues present in the sample introduction system of the ESI-IMS. Table 2 gives the molecular weight, the drift times, and the ion mobility

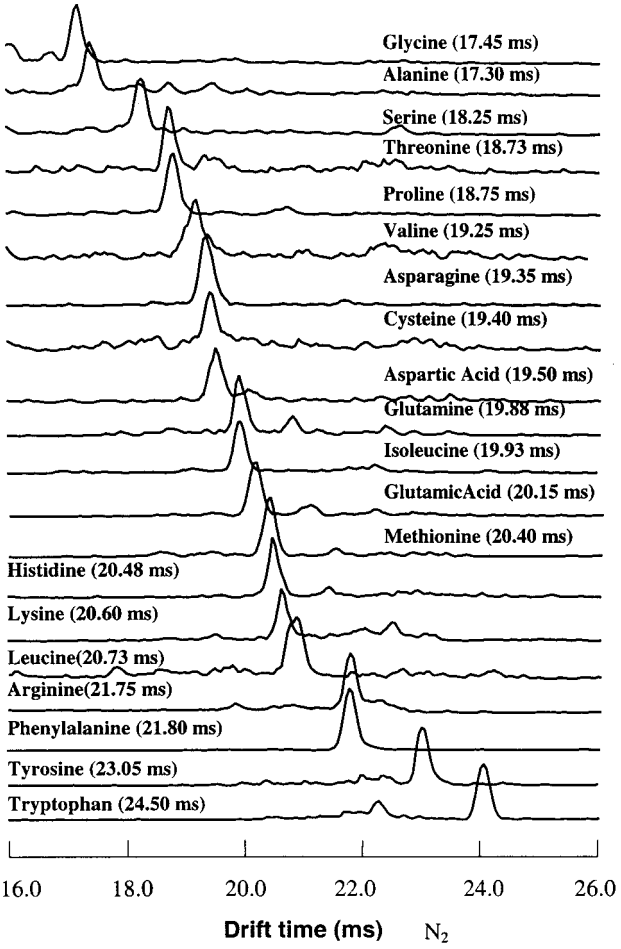

Figure 1. Ion mobility spectrum of 20 amino acids using N_2 as the drift gas.

constants (K_0^m) obtained utilizing ESI-IMS for all 19 amino acids studied with Ar, N_2, and CO_2 as a drift gas. The K_0^m values representing three different experimental configurations are tabulated, along with the values from ref 13 that were obtained on a 13-cm-length drift tube using a 4000 V drift voltage. The last two columns represent the present measurements which were carried out with the aforementioned 22.5-cm high-resolution IMS using drift voltages of 7800 and 6050 V, respectively. The drift voltages were measured using a Fluke voltmeter and were accurate to within 1% of the set voltage on the Bertan power supply. As seen from the Table, these two measurements (7800 and 6050 V) tend to agree perfectly with each other; however, when compared to those of ref 13, the present values are consistently lower (4−6%). The reason for this discrepancy is not clear.

Separation of two successive peaks is a function of both the measured peak width and selectivity (i.e., how far apart two peaks are). One can increase the selectivity in IMS by lowering the electric field value such that drift times of two successive ions increase proportionally according to the expression given in eq 1. For example, as shown in Table 2, the difference in drift times of leucine and isoleucine were increased from 0.8 to 1 ms (20%) by lowering the electric field strength from 7800 to 6050 V (~20%). Similarly, phenylalanine and arginine have drift times at 7800 V

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Table 2. Molecular Weights, Drift Times, and Ion Mobility Constants of 19 Common Amino Acids Obtained with N_2, Ar, and CO_2 as Drift Gases

amino acid	MW amu	K_0 in N_2, Asbury and Hill (2000), K_0	K_0 in N_2 $V = 7800$V DT (ms)	K_0	K_0 in N_2 V = 6050V DT (ms)	K_0	Ar V = 6400V DT (ms)	K_0	CO_2 V = 8700V DT (ms)	K_0
glycine	76	1.968	17.15	1.851	22.00	1.853	21.30	1.781	25.55	1.093
alanine	90	1.805	17.30	1.825	23.33	1.738	21.20	1.798	25.45	1.097
serine	106	1.819	18.25	1.734	23.55	1.736	22.05	1.720	27.00	1.034
proline	116	1.787	18.75	1.692	24.10	1.696	22.85	1.659	26.85	1.040
valine	118	1.721	19.25	1.639	24.70	1.644	24.20	1.566	27.90	1.001
threonine	120	1.757	18.73	1.685	24.15	1.679	22.90	1.656	27.65	1.010
cysteine	122	1.748	19.40	1.631	24.75	1.646				
isoleucine	132	1.632	19.93	1.583	25.60	1.586	25.90	1.463	28.35	0.985
leucine	132	1.618	20.73	1.526	26.60	1.531	26.30	1.441	29.25	0.955
asparagine	133	1.714	19.35	1.628	24.75	1.636	23.50	1.613	28.40	0.983
aspartic acid	134	1.704	19.50	1.616	25.05	1.619	23.60	1.606	28.70	0.973
glutamine	147	1.638	19.88	1.587	25.43	1.594	25.50	1.483	28.55	0.978
lysine	147	1.603	20.60	1.535	26.50	1.534	25.80	1.469	28.20	0.990
glutamic acid	148	1.644	20.15	1.566	25.70	1.575	25.60	1.480	28.90	0.966
methionine	150	1.597	20.40	1.546	26.15	1.550	25.50	1.486	29.00	0.963
histidine	156	1.608	20.48	1.541	26.13	1.549	25.30	1.501	28.85	0.968
phenylalanine	166	1.495	21.80	1.448	28.00	1.450	28.40	1.334	30.75	0.908
arginine	175	1.503	21.75	1.452	28.30	1.436	27.20	1.393	29.90	0.934
tyrosine	182	1.440	23.05	1.366	29.55	1.369	29.50	1.284	30.75	0.908
tryptophan	205	1.349	24.05	1.311	30.88	1.316	31.30	1.210	33.40	0.836

within 0.05 ms of each other; however, at 6050 V, that increased to 0.30 ms, at which point it was sufficient to resolve the peaks.

However, increasing drift times by reducing the electric field (voltage drop) to gain more separation between two successive ions increases the peak widths of the ions according to eq 4.[14] The measured peak width, *w*, can be represented by the expression

$$w^2 = t_g^2 + (16\,kT \ln 2/Vez)t_d^2 \qquad (4)$$

where t_d is the measured drift time, t_g is the gate width, k is Boltzmann constant, T is the temperature, V is the voltage drop across the drift region, e is elementary charge, and z is the number of charges on the ion. The effects on resolution are demonstrated in Figure 2 for methionine. As seen from the Figure 2, the width, *w*, increases by 0.04 ms (or ~15%) when the voltage drop is decreased from 7800 to 6050 V.

As seen in both Figure 1 and Table 2, many of the amino acids have similar drift times, which makes it very hard to uniquely identify two amino acid ions in a spectrum. Those molecules with similar K_0 include proline and threonine (0.4% difference using our K_0 values); asparagine and aspartic acid (0.5%); phenylalanine and arginine (0.3%); and lysine, methionine, and histidine (0.8%), which precludes them from being separated in N_2.

Because increasing the resolving power in IMS by lowering the electric field strength has an adverse effect on peak width (see eq 4), as demonstrated in Figure 2, an alternative approach can be used to improve the resolution of IMS in terms of both the peak width and the selectivity. Changing the drift gas composition can improve the ion mobility separation in IMS.[11] The selectively can change by altering two different terms: a mass-dependent one and a polarizability one.[15,11] The mass-dependent

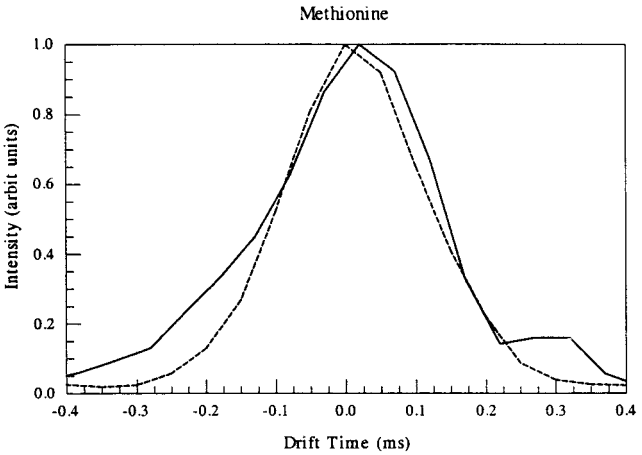

Figure 2. Spectra of methionine showing the change in resolution as the drift voltage changes from 7800 V (dashed line) to 6400 V (solid line).

term is important only for ions with molecular weights that are similar to the molecular weight of the drift gas. The polarizability of the drift gas affects the selectivity because a higher polarizability corresponds to a longer drift time for a given target ion or vice versa.

As mentioned previously, when the drift times of ions increase, their peak areas (i.e., sensitivity) decrease, but the resolving power increases.[6] This can be demonstrated by comparing the drift times of the amino acids shown in Figure 3 for Ar as the drift gas and Figure 4 for CO_2 as a drift gas. Table 2 lists the reduced mobility for all 19 amino acids in the three different drift gases and shows that the drift times for the ions in N_2 are less than those obtained in Ar, which in turn are less than the drift times in CO_2. When we compare the drift times, for example, phenylalanine and arginine in N_2 (the polarizability of N_2 is 1.74×10^{-24} cm^3), the drift times are comparable (21.80 ms for phenylalanine and 21.75 ms for Arginine), and they are practically inseparable in N_2. However, they are clearly separable in CO_2 (the polarizability of

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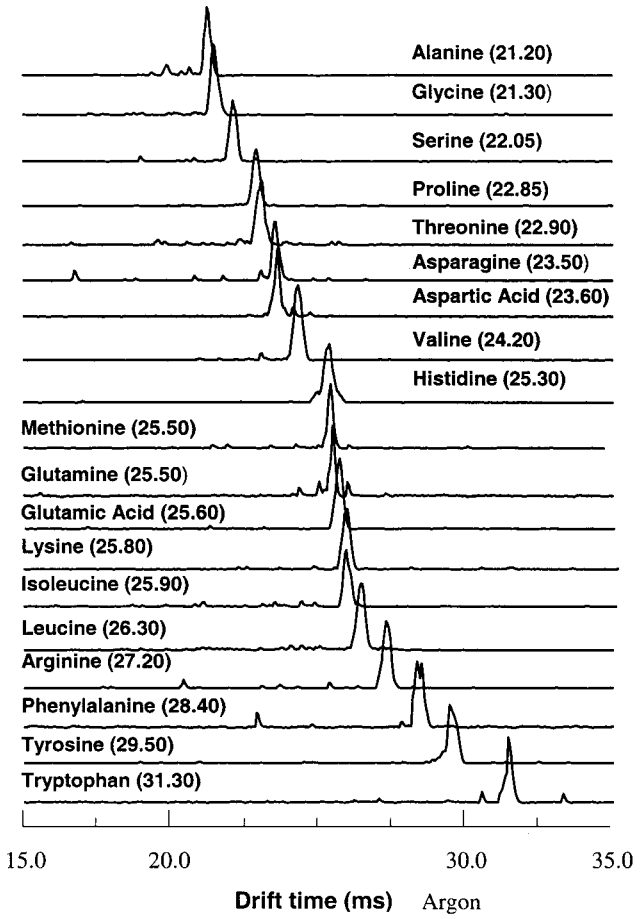

Figure 3. Ion mobility spectrum of 19 amino acids using Ar as the drift gas.

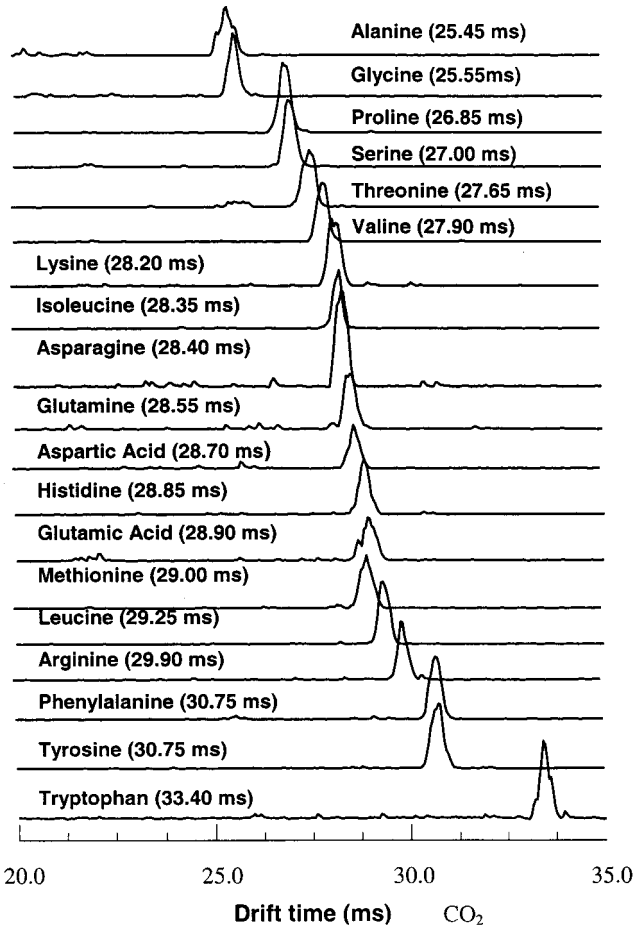

Figure 4. Ion mobility spectrum of 19 amino acids using CO_2 as the drift gas.

CO_2 is 2.911×10^{-24} cm^3), where the difference in drift times is 0.85 ms. Figure 5 demonstrates that the use of different drift gases (such as N_2 and CO_2) can drastically improve the separability of phenyalanine and arginine.

Analysis of Liquid Samples Containing Mixtures of Amino Acids. In this section, we report the result of our analysis of liquid samples containing mixtures of amino acids and demonstrate the potential of the high-resolution ESI-IMS technique as an analytical separation tool in analyzing biomolecular mixtures to pursue astrobiological objectives of searching chemical signatures of life for in-situ exploration of solar system bodies.

Four different amino acid mixtures were prepared in different concentrations. Table 3a,b lists the constituents and concentrations for each mixture. Figure 6a−d shows the corresponding ion-mobility spectra that were obtained under the same experimental conditions using N_2 as the drift gas over a two-day period.

Figure 6a,c represents mixtures of amino acids having different concentrations (higher and lower concentrations relative to each other), as seen in Table 3a. The high concentrations (20−25 ppm) were used to determine if there was any indication of charge-transfer chemistry taking place in the electrospray process. Furthermore, smaller a concentration of a sample (such as 5 ppm of threonine in Figure 6a or phenyalanine in Figure 6c, respectively) was included to determine if they would be detectable in a mixture in which charge competition may be taking place. There are no indications in the spectra that any charge-transfer chemistry

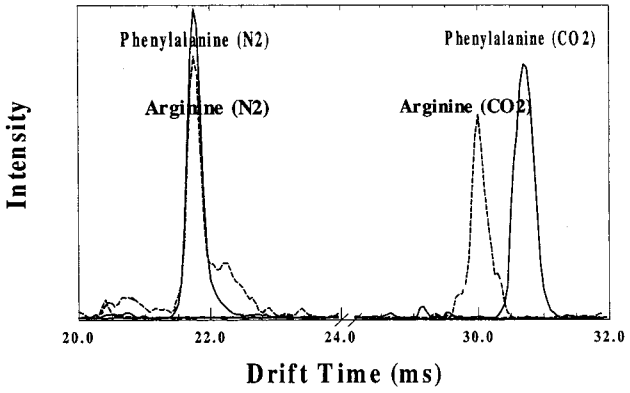

Figure 5. Overplot of ion mobility spectra of phenyalanine and arginine with N_2 and CO_2 as the drift gases. The spectra demonstrate that the use of different drift gases can drastically improve the separability.

takes place; however, there is evidence that charge competition between the different amino acids does take place, because there was no correlation in the peak intensity and the concentration, as seen from Figure 6b, in which the concentrations of all of the amino acids in the mixture are 20 ppm.

As shown in Figure 6b, leucine and histidine have similar drift times (20.27 and 20.48 ms, respectively) and are practically indistinguishable in N_2 with the resolution of ~0.3 ms used for the measurements. However, using different drift gases, such as

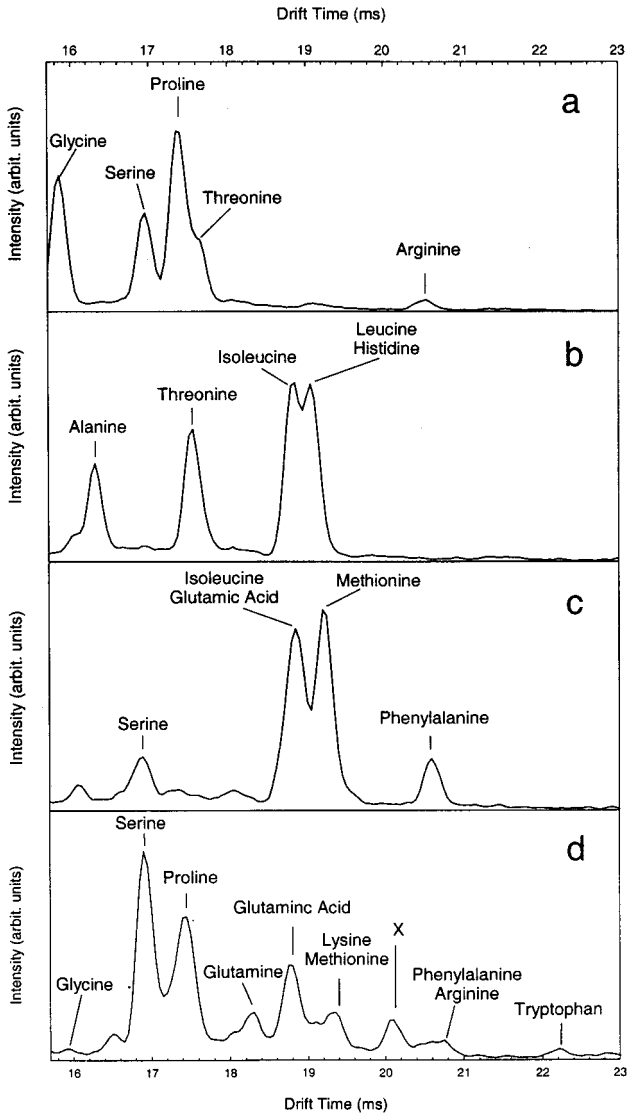

Figure 6. Composite spectra of four different mixtures run over 2 days. Peaks for each are marked with the corresponding constituent of the prepared mixture, as determined from the calculated K_0 values of each peak.

Ar or CO_2, the separability can drastically be improved, as discussed in the previous section. The differences in drift times are 1.0 ms and 0.4 ms in Ar and CO_2, respectively, as opposed to 0.25 ms in N_2. Similarly, isoleucine and glutamic acid are inseparable in N_2, where the difference in drift time is only 0.22 ms, as shown in Figure 6c; however, this can be improved approximately 2.8 to 3× if either CO_2 or Ar, respectively, is used. Of note is that an unidentified peak shown in Figure 6c (before the serine peak), which also appears on left shoulder of the alanine peak in Figure 6b, is most likely a solvent peak.

Figure 6d shows the spectra of a mixture consisting of 10 different amino acids listed in Table 3b with N_2 as a drift gas. The sample concentration for each was 10 ppm. The figure shows the 8 distinctive peaks, with methionine/lysine and phenylalanine/arginine samples indistinguishable from each other, which is expected from the drift times listed in Table 2. As in the samples shown in Figure 6a,c, there is no correlation in the peak intensity and sample concentration. The noise in the spectra can be attributed to either slight contamination in the sample loop or the result of charge transfer in the drift cells between neutral amino acids and ions. The unknown feature, labeled "X", in the mixture is probably a contaminant, because the experimental apparatus (i.e., ESI-IMS) is open to environmental contaminants. The same unknown peak showed up in other subsequent spectra (which are not shown here) for other mixtures.

Table 3. Listing of the Amino Acids and Their Concentration Present in Each of the Mixtures Shown in Figure 6

amino acid	concn, ppm
Mixture 1 (Figure 6a)	
glycine	25
serine	20
proline	10
threonine	5
arginine	10
Mixture 2 (Figure 6b)	
alanine	20
threonine	20
isoleucine	20
leucine	20
histidine	20
Mixture 3 (Figure 6c)	
serine	10
isoleucine	20
glutamic acid	12
methionine	25
phenylalanine	5
Mixture 4 (Figure 6d)[a]	
glycine	10
serine	10
proline	10
glutamine	10
lysine	10
glutamic acid	10
methionine	10
phenyalanine	10
tryptophan	10
arginine	10

[a] Corresponding ion-mobility spectrum shown in Figure 6d.

SUMMARY AND CONCLUSIONS

The ion mobilities of 19 common amino acids were determined by electrospray ionization ion mobility spectrometry using three different drift gases (N_2, Ar, and CO_2). We demonstrated that the selectivity can be vastly improved in IMS by using different drift gased when detecting organic molecules. Using different drift gases in ion mobility spectrometry has a number of significant effects on the separability of ions because of interactions with the drift gas. The polarizability and mass of the drift gas affects the drift times of ions. The polarizability effect changes the calculated ion radii in a linear fashion, with each ion studied having a different slope.[11] However, when using a heavier gas to increase the separability of ions, the heavier gas causes an increase in the drift time, which causes a decrease in the resolution. This can be overcome by increasing the voltage applied to the drift length. Because of the differences in polarizability of different molecules, it is possible to determine the identity of each of them uniquely, with the exception of alanine and glycine, which are polarized the same in each of the drift gases studied here.

We also report the result of our analysis of four different amino acid mixtures prepared in different concentrations. We were able to identify the constituents in these mixtures by using the ion tables generated with different drift gases. The present investigation indicates that the high-resolution ESI-IMS technique has a potential to be a stand-alone analytical separation tool that can be utilized in a chemical environment containing organic samples in pursuing astrobiological objectives of searching chemical signatures of life for in-situ exploration of solar system bodies. Laboratory measurements are in progress to determine the K_0 values of more complex organic molecules, such as mononucleotides and fatty acids, in different drift gases to further demonstrate the potential of the high-resolution ESI-IMS technique for detecting and accurately analyzing a mixture of organic compounds. Organic molecules present on Mars most likely have undergone some form of transformation over the billions of years the molecules existed on the near surface; therefore, investigations of the assumed derivatives of the amino acids are also underway.

One advantage of the ESI-IMS technique is that it can be easily operated to detect either positive ions (as described here) or negative ones. When a complex sample is introduced, constituent molecules become preferentially ionized in either positive or negative modes by the ESI process, so not every molecule is ionized in each run. This process, thus, reduces the number of ions detected in each run, making the obtained spectra less complex, and thus, easier to analyze, so by switching between positive and negative modes, the amount of information about a sample can be greatly increased.

It is possible that a small, self-contained ESI-IMS instrument with several reservoirs of drift gases would be to able to quickly detect and correctly identify organic compounds (such as the amino acids studied here) as part of an in situ experiment on the surface of a planetary body such as Europa.

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