COULOMB REPULSION IN MINIATURE ION MOBILITY SPECTROMETRY

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Abstract: We have undertaken a study of ion mobility resolution in a miniature ion mobility spectrometer with a drift channel 1.7 mm in diameter and 35 mm in length. The device attained a maximum resolution of 14 in separating ions of NO, O₃, and methyl iodine. The ions were generated by pulses from a frequency-quadrupled Nd:YAG laser. Broadening due to Coulomb repulsion was modeled theoretically and shown experimentally to have a major effect on the resolution of the miniature device.

INTRODUCTION

Miniaturization of ion mobility spectrometry (IMS) can potentially lead to pocket-sized devices that deliver information about ambient chemical species [1]. As the ion drift channel is reduced, it becomes increasingly difficult to achieve diffusion-limited resolution. Possible technical barriers include inhomogeneous drift field, charging on the channel surface, enhanced space-charge effect due to the reduced volume, and relatively large reaction region. This paper presents studies on these technical aspects with a focus on resolution degradation by space charge in miniaturized IMS.

COULOMB REPULSION

Resolution (R) is generally defined as the ion drift time (tᵢ) divided by the full width at half maximum (w) of the ion peak detected. Factors that determine resolution include: (1) initial ion pulse width [2], (2) spatial broadening by diffusion of the ion packet, (3) broadening by Coulomb repulsion between ions in both the ionization and drift regions [3, 4], and (4) inhomogeneous drift field. As to be discussed later, the inhomogeneous effect can be neglected. Then the resolution can be expressed in three major components:

\[
\frac{1}{R^2} = \frac{1}{R_i^2} + \frac{1}{R_D^2} + \frac{1}{R_C^2}
\]  \hspace{1cm} (1)

where

\[
R_i = \frac{L^2}{\Delta \tau KV}
\]  \hspace{1cm} (2)

\[
R_D = \sqrt{\frac{zeV}{16 \ln 2kT}}
\]  \hspace{1cm} (3)

where L is the drift length, \(\Delta \tau\) includes the initial ion pulse width, K is the mobility of the ion, V is the drift bias, \(z\) is the charge state of the ion, e is the charge of electron, k is the Boltzmann constant, and T is the drift temperature in Kelvin.
Laser ionization was adopted for testing miniature IMS systems because of its simplicity. [7] The laser radiation was focused into a small region with enough intensity for multiphoton ionization of the analytes. However, this small region can generate a relatively large amount of Coulomb repulsion. Considering the effective volume of the laser ionization as a cylinder with an initial radius of $r_0$ (0.2 mm) and a length of $h$ (3 mm), using Gauss' law, the electric field, $E_r$, induced by space charge at the edge of the ion cylinder is

$$E_r = \frac{Nze}{2\pi \varepsilon_0 hr}$$

(4)

where $N$ is the total number of ions per laser pulse, $\varepsilon_0$ is the permittivity of free space. $N$ is estimated to be about 1 million ions per pulse for the 0.1 mJ laser power used, therefore $E_r$ is ~ 50 V/cm. This field is comparable to the drift field, which is about 200 V/cm. Ions are expanded by the space charge field in the radial direction by a velocity,

$$\frac{dr}{dt} = KE_r$$

(5)

while they are drifting toward the detector with velocity, $V_d = K E_d$. Substituting Eq( ) and solving this differential equation for ions drifting from the location of the laser beam to a distance $L$, we obtain Coulomb repulsion component of resolution,

$$R_c = \frac{t_d}{\Delta t_c} = \sqrt{\frac{\pi \varepsilon_0 hV}{Nze}}$$

(6)

**EXPERIMENTAL**

Figure 1 shows the image of the miniature IMS, which consists of a 1.7 mm diameter drift channel, 35 mm in length. The channel is comprised of 25 stacked copper lenses separated by Macor spacers and mini resistors with a total resistance of 20 MΩ. The Macor spacers have a larger inner diameter than that of the copper lenses, which minimizes the charging of the internal surface of the column. The IMS device is combined with two 35-W cartridge heaters (Omega) and a thermocouple for controlling the temperature in a range between 22°C and 150°C.

The apparatus was baked at 120°C overnight in a flowing Ar atmosphere to minimize background ions. Sample gas was introduced through a mass-flow controller (MKS-10 sccm) with a flow rate of 7.5 sccm. Sample gases used were 0.8 ppm NO in Ar, CH₃I vapor from a liquid tube, and O₂ and H₂O impurities in the N₂ drift gas, or their mixture. The N₂ drift gas was purified by a filter (LABCLEAR) and regulated at a maximum of 500-sccm flow rate. The drift gas passed through a specially designed spiral channel and then flowed in a reverse direction to the ion flow. The spiral channel was made in such a way that it yielded a 900 mm flow length inside the 35 mm length IMS. This spiral channel allowed the drift gas to reach an equilibrium temperature with the spectrometer prior to entering the drift channel. Sample gas, carrier gas, and drift gas exited from the ionization region through a valve attached to a pump which controlled the pressure in the IMS in the range between 380 torr and 1000 torr.

Ultraviolet laser radiation (266 nm) from a Nd:YAG laser (Quanta-Ray) or from an excimer laser (248 nm, MPB) entered the ionization region through a quartz window,
intercepted the sample gas, and exited through another quartz window. The laser pulse width from the Nd:YAG laser was 5 ns and the repetition frequency was 10 Hz. The laser radiation permitted direct ionization of molecules, minimizing the problem of non-specific ionization as with $^{63}$Ni radioactive sources. Laser photoionization provides extremely efficient ionization for large molecules with primarily molecular ions being formed. [5, 6]. The laser was operated with an energy of less than 0.1 mJ/pulse and the beam was focused to a spot ~0.4 mm in diameter in the ionization region for most of the measurements. To ionize NO molecules, a two photon process is needed. The free electrons generated by photoionization were captured by NO, O$_2$ and CH$_3$I to form negative ions. The excimer laser, with a maximum energy of 1.6 mJ/pulse was used for a study of output pulse duration as a function of laser pulse energy.

Ions were separated in the drift region according to their mobilities and reached a Faraday cup located at the end of the IMS channel. A grid was mounted in front of the detector plate and ac-grounded through a capacitor so the electric current due to ion movement would not be coupled to the detector. The current collected by the plate was amplified through a high-sensitivity pre-amplifier. The signal was sent to a Tektronix digital oscilloscope and a PC computer running Labview software.

The homogeneity of the drift field is one of factors in affecting resolution. To have a homogeneous field, we adopted 25 lenses in such a short channel. These lenses are biased by external potentials linearly divided according to their distances to the detector. The diameter of copper lens is smaller than that of Macor insulator, so that the surface charging on the insulator does not significantly affect the drift potential. A SIMION [7] calculation was used to evaluate the potential produced in the drift region. Figure 2 shows the calculated potential as a function of the longitudinal distance at the center of the channel. The potential is a straight line within 0.1% deviation, which is much smaller than the 1% variation introduced by the uncertainty of the miniature resistors. The SIMION calculation also yielded the potential as a function of distance in the radial direction, which decreases as the radius increases, however not exceeding 0.1% variation.

RESULTS AND DISCUSSION

Figure 3 shows ion mobility spectra of negative ions detected by the miniature IMS under laser radiation of NO, NO + impurity, and NO + impurity + CH$_3$I mixtures. In Fig. 3(a) a single peak appears as 0.8 ppm nitric oxide was introduced into the ionization region. The gas pressure in the drift region was adjusted to about 1 atmosphere and the drift potential was -500V. NO molecules are ionized by a two-photon ionization process, while the background Ar was not ionized under the current laser conditions. The free electrons that were liberated by photoionization were captured by NO since the molecule has a positive electron affinity (0.025 eV).

After adding the N$_2$ drift gas, two ion peaks appeared in the IMS spectrum, as shown in Fig. 3(b). The later peak is attributed to NO$^-$ since its intensity varied accordingly to the NO flow rate. The earlier peak is believed due to residual O$_2$ in the drift gas. As the flow rate of the drift gas was increased, the earlier peak intensity increased accordingly. The initial N$_2$ gas was contaminated by 1.2 ppm oxygen and 1.1 ppm of moisture. After passing through the filter, the impurity concentration was approximately 50 ppb.
The ddrd peak is displayed in Figure 3(c) as CH₃I gas was added to the ionization region. The new peak is attributed to CH₃I, which has an electron affinity of 0.3 eV. The drift potential was -800V. The CH₃I molecules were generated from the evaporation of liquid CH₃I from a vial that was attached in the sampling line. The concentration was estimated to be a few tens of ppb. Since the three spectra were obtained at different pressures and different biases, which affect the mobility of the samples, we rescaled the drift times in (a) and (b) to that of (c).

As indicated in Eq. (6), the Coulomb contribution to the resolution depends on the total number of ions initially generated and thus should vary with the energy of the ionization laser pulse. We measured the resolution as a function of laser energy for different drift biases, as shown in Figure 4. For each bias, the resolution was found to be lower at higher laser pulse energy. This effect was significantly larger at the lower bias voltage. For a field higher than that generated by -600V, the initial time spread dominates the resolution and the effect of Coulomb repulsion is less important.

CONCLUSIONS

We have presented the results of studies of a miniature ion mobility spectrometer (IMS) that has a drift channel a 1.7 mm diameter and a 35 mm length. The miniature IMS has been characterized by measuring both negative and positive ion spectra produced by a frequency-quadrupled Nd:YAG laser on samples of NO, O₂, and methyl-iodide. The device demonstrates useful resolution and high sensitivity, using a low operating voltage. Broadening induced by Coulomb repulsion was theoretically studied and experimentally demonstrated to have a major effect on the resolution of the miniature device.

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REFERENCES

Figure 1. Image of miniature ion mobility spectrometer that has a drift channel 1.7 mm in diameter and 35 mm in length.
Figure 2. Potential as a function of the longitudinal distance, calculated with SIMION [7] program.
Figure 3. Ion mobility spectra of negative ions generated under laser radiation of (a) NO, (b) NO + impurity, and (c) NO + impurity + CH₃I mixtures.
Figure 4. Instrumental resolution as a function of laser pulse energy for different drift biases.