Development of an Off-axis Sample Introduction System for Use in Multiphoton Ionization/Time-of-flight Mass Spectrometry

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An off-axis sample introduction technique was developed for improvement of mass resolution in multiphoton ionization/time-of-flight mass spectrometry. The direction of the capillary for sample introduction was inclined 30° relative to the axis of ion trajectory in the time-of-flight tube for both selective and sensitive detection. This approach suppressed the excessive collisions between analyte ions and carrier gas molecules that is responsible for degradation of mass resolution.

Multiphoton ionization/time-of-flight mass spectrometry (MPI/TOFMS) combined with a supersonic jet is a highly selective analytical technique.[1–3] Typically, the direction of the electric field vector of the ionization region is perpendicular to the direction of sample introduction. In contrast, we developed a collinear ionization source, i.e., the direction of sample expansion was tangential to the ion trajectory in the time-of-flight tube.[4] In this sample introduction technique, analyte molecules are directly introduced through a repeller electrode that is connected to a pulsed nozzle. The advantages of the collinear ionization technique are as follows: the nozzle can be adequately heated, and the distance between the nozzle and the ionization region can be reduced. Because the analyte molecules can be ionized at high densities behind the nozzle, ionization efficiency is improved. This method has been applied to continuous sample introduction using a capillary column as a nozzle.[5] Very recently, sample introduction using both the collinear configuration and analyte adsorption/laser desorption was reported to increase the signal intensity by two orders of magnitude.[6] Therefore, this system is very useful for enhancement of the sensitivity of the detection. However, with continuous sample introduction, ions induced by the ionization laser collide excessively with the carrier gas, because their directions are collinear. An increase in the distribution of both the velocity and direction of the ions, especially in the ion-acceleration region, degrades mass resolution by increasing the duration of the flight time. Therefore, the experimental conditions, e.g., laser alignment and flow rate of the carrier gas, have been carefully optimized to achieve mass resolution >1000. In the present study, changes in mass resolution resulting from alterations in the position of the ionization region were quantified. Moreover, a new sample introduction technique, i.e., an off-axis sample introduction system, was developed, in which the advantages of conventional collinear ionization, e.g., heatability and sensitivity, were preserved, while the disadvantage—a decrease in the mass resolution—was improved.

Figure 1 shows a schematic diagram of the experimental apparatus used in this study. Details of the MPI/TOFMS instrument have been reported elsewhere[7,8] and are only briefly described here. A sample of chlorobenzene was placed in a reservoir. The sample was then introduced into a homemade linear TOFMS using a capillary column (capillary length: 1 m; i.d.: 0.25 mm), which acts as an effusive molecular beam. The flow rate of the carrier gas (air, 1.0 mL min^{-1}) was controlled using a flow meter to maintain a constant concentration. The direction of the capillary attached to the vacuum chamber was either tangential (0°) or inclined 30° relative to the axis of ion trajectory in the flight tube. The collinear and off-axis configurations could be interchanged by replacement of the capillary holder. The pressure in the chamber was 3.5×10^{-3} Pa at a flow rate of 1.0 mL min^{-1}. The third harmonic emission (TH) of a Ti:Sapphire laser (Coherent, Libra, Fundamental: 800 nm, 80 fs, 1 mJ, 1 kHz, TH: 267 nm, 150 μJ) was employed as the ionization laser. The energy was reduced to ca. 20 μJ using a variable aperture (iris diameter, 2 mm). The laser was focused using a fused-silica lens (focal length, 300 mm), so that the diameter of its beam was ca. 50 μm in the ionization zone. The applied potential of a repeller- and first-extraction-electrode were adjusted to achieve optimum mass resolution during each experiment. The induced ions were detected using an assembly of microchannel plates (Hamamatsu, F4655-11). Each mass spectrum was measured 2000 times, and the signals were averaged using a digital oscilloscope (Tektronix, DPO5104, 1 GHz, 5 GS s^{-1}). All experiments were carried out at room temperature.

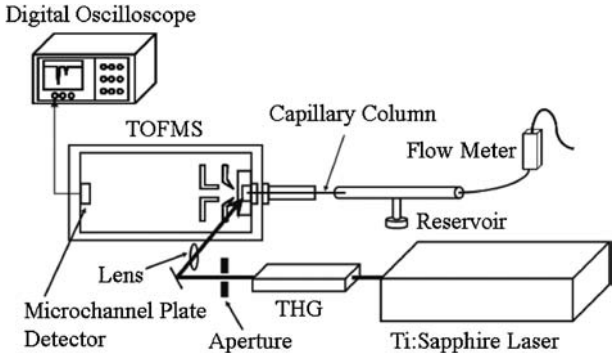

Figure 1. Schematic diagram of the experimental apparatus. THG: Third harmonic generator.

Figure 2 shows the mass spectra for chlorobenzene obtained using the collinear configuration. When the laser was introduced directly below the nozzle, the mass resolution for the molecular ion peak observed for m/z 112 was 290, as shown in Figure 2a. An increase in the mass resolution of up to 650 was observed (Figure 2b) when the ionization spot was moved ca. 2 mm

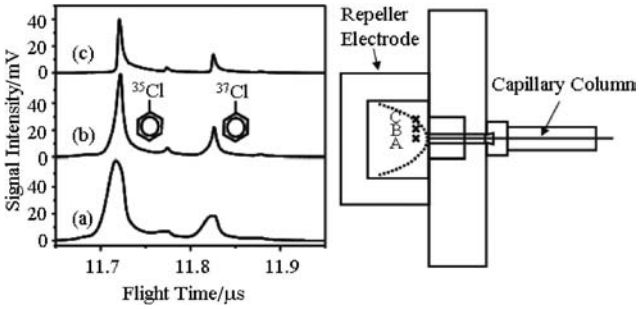

Figure 2. Mass spectra for chlorobenzene obtained using the collinear configuration. Each spectrum (a), (b), and (c) corresponds to the ionization spot denoted by the corresponding "×" (A to C) on the right side of the figure.

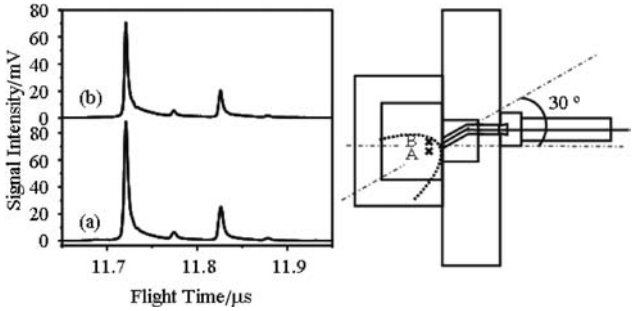

Figure 3. Mass spectra for chlorobenzene obtained using the off-axis configuration. Each spectrum (a) and (b) corresponds to the ionization spot denoted by the corresponding "×" (A and B) on the right side of the figure.

(Figure 2b) above center (Figure 2a), while maintaining a nearly constant signal intensity. As a result, the decrease in the concentration of sample molecules in the ionization region affected the decrease in the area of ion signal. These results suggest that excessive collisions between the ions and the neutral species occurred (Figure 2a), and that the number of collisions was reduced at lower carrier gas densities. In the collinear configuration, a mass resolution of up to 1200 was achieved when the spot was moved ca. 4 mm above center (Figure 2c). However, the signal intensity decreased by ca. 65% compared to that obtained in Figures 2a and 2b. In the same manner, a mass resolution of greater than 1000 was achieved only when the signal intensity was reduced by 50–70%.

To suppress excessive collisions between ions and carrier gas, the direction of the capillary was inclined 30° relative to the axis of ion trajectory in the flight tube (Figure 3). A mass resolution of 1200 was achieved with maximal signal intensity using this experimental set-up (Figure 3a). The signal intensity was 2.3-fold greater than that obtained using the collinear configuration with the same mass resolution (Figure 2c). Moreover, the off-axis configuration improved the mass resolution to 1500 when the ionization spot was moved ca. 2 mm (Figure 3b) above center (Figure 3a). However, the signal intensity was reduced by ca. 80%. These results imply that collisions between analyte ions and neutral gas molecules are negligible in this configuration. In the present study, the signal peak for chlorobenzene should have a full width at half-maximum (FWHM) of less than 4 ns to achieve a mass resolution, $m/\Delta m$, equal to $t/2\Delta t$ in TOFMS of 1500. Therefore, the femtosecond pulsed laser used in this study effectively improved mass resolution compared with nanosecond lasers used in conventional laser ionization. The mass resolution obtained by use of both the linear TOFMS and the off-axis sample introduction method was comparable to mass resolution (500–1800) typical of conventional reflectron TOFMS using laser ionization.[9–14] Moreover, an interesting application of the linear TOFMS method is measurement of the initial kinetic energy distributions of ions, which should be compensated for by the use of the reflectron.

In conclusion, we developed an off-axis sample introduction technique to suppress excessive collisions between analyte ions and carrier gas molecules. As a result, the signal intensity was enhanced approximately 2-fold relative to that obtained using the collinear configuration with compatible mass resolution (ca. 1500). The off-axis system has the potential for use in trace analysis of target compounds due to its high selectivity, sensitivity, and good heatability.

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