Development of a tabletop time-of-flight mass spectrometer with an ion attachment ionization technique

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We report a new type of mass spectrometry based on a time-of-flight mass spectrometer combined with an ion attachment ionization technique (IA-TOF). In contrast to electron ionization mass spectra, IA-TOF mass spectra are not complicated by peaks due to fragmentation of the molecular ion; the adduct ion formed in IA does not fragment. We developed a tabletop IA-TOF system and evaluated its performance by analyzing specimens originally in the gas, liquid, and solid phases. We obtained fragment-free spectra covering a mass range up to \( m/z \) 3400 with a mass resolution of about 4700. Our IA-TOF system realizes accurate and versatile real-time mass spectrometry. Copyright © 2007 John Wiley & Sons, Ltd.

Gas chromatography (GC), electron ionization (EI), and quadrupole mass spectrometry (QMS) are combined and widely applied in conventional mass spectrometry of gas-phase organic molecules. However, two important problems complicate the routine use of GC/EI-QMS.

First, EI mass spectra of organic molecules are routinely acquired at an impact energy of 60–80 eV because the ionization efficiency versus electron energy curves generally show a maximum around 70 eV, where the highest ionization efficiency and best reproducibility of the spectra are assured. However, because most molecules have a relatively low ionization energy (7–15 eV), the excess energy on EI may lead to dissociation of the organic molecules and production of complex fragment ions. Consequently, although EI-MS has long been a standard method for analysis of molecular structures, it provides only poor information on molecular mass.

For analysis of multicomponent samples, GC pre-separation can be used to isolate a single species, which can then be identified by EI-MS. However, GC requires a certain level of volatility and thermal robustness of the sample molecules. In addition, GC is time-consuming and cannot be applied to real-time and on-line measurements.

Second, although the QMS system is a convenient mass analyzer, it has some disadvantages: (1) a narrow mass range, (2) mass dependence of transmission efficiency, and (3) a low mass resolution.

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So far, because of their limited mass range and low transmission efficiency for the high-mass range, most conventional QMS instruments have been capable of analyzing only species with mass-to-charge ratio below \( m/z \) 1000. Moreover, conventional instruments have a low mass resolution and are able to distinguish only nominal masses. Except for \(^{12}\text{C}\), the atomic mass of an atom is very close to, but not equal to, the nominal mass of that atom. By using mass spectrometry with a sufficiently high mass resolution, one can distinguish isobaric ions with the same nominal mass but different exact masses and identify the empirical formula of a molecule. To overcome the main disadvantages of GC/ EI-QMS systems, a new mass spectrometry system is needed.

Ionization methods that produce molecular ions and no, or only a few, fragment ions are termed soft ionization methods. Because determination of molecular mass is a key part of elucidation of the structure of unknown molecules, many soft ionization methods have been developed.¹ The first was field ionization (FI), by which gas-phase sample molecules are ionized spontaneously in a strong electric field. In FI, unlike EI, no excess energy is transferred to the incipient ions, and thus dissociation of the ions is minimized. Field desorption (FD) is a modification of FI in which sample molecules are supplied directly to the surface of a field emitter and evaporated, and then efficiently ionized in a strong electric field in the vicinity of the field emitter. FD is one of the softest ionization methods for biomolecules with molecular masses less than 3000 u, but it cannot be used to analyze gas-phase samples. FI and FD have the disadvantage

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that they produce a variety of ions, such as $M^+$, $M^{2+}$, $[M + H]^+$ and $[M + \text{Alkali}]^+$, depending on the polarity of the samples and on the presence of impurities.

Chemical ionization (CI) has become very popular for structure elucidation. CI relies on the interaction of reactant ions with neutral sample molecules and the subsequent production of new ions with internal energy much lower than that of the molecular ions produced by EI. CI involves the transfer of an electron, a proton, or some other charged species between reactants. Charge-exchange or electron-capture CI mass spectra generally exhibit molecular ions and some primary fragment ions. Protonation CI produces $[M+H]^+$ ions. In cases in which the proton affinity of sample molecule $M$ is lower than that of the reactants, $[M–H]^–$ negative ions are produced. In methane CI mass spectra, $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$ ions are sometimes observed in addition to the $[M+H]^+$ ions.

Methods for soft ionization at atmospheric pressure (AP) have also been developed. The excess energy of the ionization process can be removed by collisional quenching with gas, such as nitrogen or air. In the AP photoionization (APPI) method, choosing the proper proton energy by means of lasers and vacuum-UV lamps permits reasonably selective ionization. APCI can be used to ionize non-polar molecules in addition to polar molecules.

The FI, FD, CI, APPI, and APCI soft ionization methods provide molecular mass information, but their sensitivity depends strongly on the characteristics, such as polarity, affinity, and ionization energy, of the sample molecules.

A new CI method—the ion attachment (IA) method—has been evaluated. In IA, an alkali metal ion $A^+$ attaches to a sample molecule $M$. These ion association reactions are described as follows:

$$M + A^+ \leftrightarrow [M + A]^{++} \quad (1)$$

$$[M + A]^{++} + N_2 \leftrightarrow [M + A]^{++} + N_2 \quad (2)$$

Because the excess energy of the attachment process is lower than the binding energy of the sample molecules, the adduct ions $[M+\text{Alkali}]^+$ do not dissociate. As a third body, $N_2$ introduced in the environment removes the excess energy to stabilize the adduct ion $[M+\text{Alkali}]^+$ for mass analysis. With IA, only one peak appears in the mass spectrum, corresponding to one component. Fragment-free ionization enables mass measurement of multicomponent samples without pre-separation. IA can ionize both polar and non-polar molecules with sensitivity sufficiently high for mass analysis.

The disadvantages of QMS systems described above may be overcome with time-of-flight (TOF) mass spectrometers, and the ions can be investigated over a wide mass range with a high mass resolution.

We have been developing a new TOFMS system employing IA (IA-TOF). Although high mass resolution generally requires a bulky TOFMS apparatus, we have attained high mass resolution with a relatively compact tabletop IA-TOF system. We have evaluated the performance of our system by measuring several specimens originally in the gas, liquid, and solid phases. In this paper, we describe the basic concepts of the IA-TOF system and our measurement scheme, and report experimental mass spectra of various samples.

**DEVELOPMENT OF THE TABLETOP IA-TOF SYSTEM**

The IA-TOF system mainly consists of an IA ion source, a differential pumping system, and a TOF mass spectrometer (Fig. 1). The main body of the IA-TOF system is a tabletop size (50 cm × 80 cm).

**IA ion source**

The IA ion source was developed based on that adapted to QMS systems by Fujii et al. We used lithium (Li) as the alkali metal since the lithium ion has the highest affinity energy among the alkali metal ions. The IA ion source consisted of a Li emitter and an aperture. The Li emitter, a small bead of Li aluminosilicate mounted on an iridium filament wire, was placed at a distance of 15 mm from the aperture. Unless corrosive samples are used, the emitter lasts for approximately 100 h. A steady electric field ($E = 10$ V/cm) was applied to control kinetic and internal energies of $Li^+$ ions and adduct ions in the ion source.

The $Li^+$ ions were produced by electrically heating the Li emitter and were cooled in an ambient third-body gas ($N_2$, 100 Pa). Gas-phase sample molecules $M$ introduced into the IA ion source were ionized by the $Li^+$ ion attachment and formed $[M+Li]^+$ adduct ions. The Li ions and the adduct ions were extracted with the $N_2$ gas through a 0.8-mm-diameter aperture and introduced into a differential pumping region. The first step in production of the adduct ions is brought about by ion-dipole or ion-induced dipole attraction between

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the Li+ ions and a sample molecule. The cross section of the interaction between an ion and a sample molecule varies inversely as the square root of the ion energy. Because Li+ ions have low energy, the cross section is a few ten times larger than that between a neutral atom and a sample molecule. The residence time of the Li+ ions in the ion source was about 3.7 × 10−8 s because the mobility of Li+ ions in N2 is reduced to about 4 cm2/V·s. Using the Wannier equation, we estimated the mean kinetic energy and the effective temperature of the Li+ ions to be 4.6 × 10−2 eV and 530 K, respectively. The emission current of the Li+ ions was about 1 × 10−8 A. Therefore, abundant Li+ ions remained in the ion source long enough to attach to the sample molecules. Our preliminary simulations showed that a Li+ ion collides with N2 molecules about 1000 times in the ion source. Therefore, a Li+ ion collides with a sample molecule approximately once in the ion source when the concentration of the sample molecule is 0.1%. This estimation shows that the emission current of Li+ ions determines the upper limit for the production of adduct ions in our IA source.

The second step of the production of adduct ions is Li+ ion capture by a sample molecule. The Li+ affinity energy depends on the polarity of the sample molecule but has a positive value. The sample molecule M can capture a Li+ ion without any activation energy to yield an adduct ion [M+Li]+. Since the excess energy, including the mean kinetic energy of the Li+ ions and the Li+ affinity energy, is lower than the binding energy of the sample molecules, the adduct ions [M+Li]+ do not dissociate.

The third step of adduct ion production is stabilization of the adduct ions. The excess energy of the attachment process is removed by collisional cooling with the ambient N2 gas, resulting in stabilized adduct ions. Although the stabilized adduct ions also collide with the ambient N2, they do not dissociate, because the mean kinetic energy is lower than the affinity energy.

A steady electric field was applied to control movement and energy of Li+ ions and adduct ions in the ion source. The energy and residence time of the Li+ ions at a low electric field are lower and longer, respectively, than the energy and residence time at a high electric field. However, a lower electric field cannot extract adduct ions effectively, because of the space-charge effect and ion loss. Ion loss is mainly due to flow and diffusion to walls.

**Differential pumping system**

To cool the lithium ions emitted from the lithium emitter and stabilize the adduct ions, we filled the IA ion source with N2 gas (100 Pa). However, we simultaneously needed to keep the TOF instrument at a high vacuum. We therefore adopted a differential pumping system with ion-transporting optics as an interface between the IA ion source and the TOF analyzer. The differential pumping and acceleration regions of the TOF mass spectrometer were separated by a 1-mm-diameter skimmer. The differential pumping, acceleration, and TOF drift regions were evacuated by 350, 300, and 300 L s⁻¹ molecular turbopumps, respectively. Typical pressures in the differential pumping, acceleration, and TOF drift regions were 1 × 10⁻¹, 3 × 10⁻⁴, and 5 × 10⁻⁵ Pa, respectively.

The adduct ions were transported by a guiding electrostatic field between the aperture at a DC potential and the skimmer at ground potential. The adduct ions that passed through the skimmer were focused on the starting point in the acceleration region of the TOF mass spectrometer by an Einzel lens. Scattering of the adduct ions by collision with N2 gas at the aperture and in the differential pumping region introduced spreads of the initial position and initial velocity (energy) at the acceleration region that reduced mass resolution.

**Orthogonal acceleration reflector TOF mass spectrometer**

A TOF mass spectrometer mainly consists of a single-stage accelerator, ion-focusing optics, a two-stage reflector, and an ion detector. Ions are accelerated by a pulsed electric field in the accelerator, then pass through a field-free TOF drift region, are reflected by the reflector, and finally reach the detector. If all the ions have the same flight path and the same kinetic energy, their time-of-flight, tTOF, from the acceleration point to the detection point is proportional to the square root of the mass m.

The mass resolution R of a TOF mass spectrometer is defined by the ratio of m to the detectable mass difference Δm:

\[ R = m / \Delta m = t_{TOF} / 2 \Delta t \]  \hspace{1cm} (3)

where Δt is the temporal broadening width of the TOF profile.

We have previously examined and demonstrated the design principle of compact TOFMS systems with high mass resolution. One can attain moderately high mass resolution even with relatively small TOFMS systems by reducing Δt to a sufficiently low level.

The dominant factors that limit the mass resolution of the present IA-TOF system are (a) the spread of the initial positions of the ions in the acceleration region, (b) the spread of the initial velocities (energies) of the ions in the acceleration region, (c) the temporal fluctuation of the electric fields of the ion-focusing optics and the reflector, (d) the fidelity and jitter of the pulsed acceleration electric field, and (e) the temporal response of the detection system.

Factors (a) and (b) cause a spread in the kinetic energy after acceleration. In addition, factor (a) also introduces a spread in the flight length in the accelerator. A reflector scheme can effectively compensate for the spread of the TOF due to the spread of the kinetic energy. To further compensate for the effect due to factor (a), we used a two-stage reflector, compensating for both first- and second-order effects of initial position variation.

To reduce the effect of factor (b), we adopted an orthogonal acceleration configuration with a high acceleration potential. The initial velocity of the ions consists of x, y, and z components (see Fig. 2). The orthogonal acceleration configuration eliminates the z component of the initial velocity parallel to the acceleration direction. The reflector further reduces the effect of the residual broadened z component of the initial velocity to a negligible level. In addition, a high acceleration potential Ud of up to 20 kV suppresses turn-around effects in the accelerator. The y component of the initial velocity in the TOF instrument is corrected by the reflector. The z component of the initial velocity is eliminated in the orthogonal acceleration configuration.
This is why we have employed a relatively high acceleration potential, enabling the design of spectrometers capable of operating over a wide mass range at high mass resolution, however, can be improved by increasing the detection efficiency for large-mass ions. We typically used higher acceleration potentials attain higher detection efficiencies and a wider mass range but lower mass resolution for small-mass ions.

An addition advantage of orthogonal acceleration is a very low background noise level of the TOFMS signals, because the ions continuously effused from the IA ion source are hindered from penetrating the TOF drift region of the TOF mass spectrometer.

Although in principle there is no upper limit on the mass range of the TOFMS system, the practical mass range is restricted by the detection efficiency of the detector. Detector efficiency, however, can be improved by increasing the acceleration potential, enabling the design of spectrometers capable of operating over a wide mass range at high mass resolution. This is why we have employed a relatively high acceleration potential \( U_a \) (up to 20 kV) in our system.

The single-stage accelerator consists of a repeller electrode and a grounded electrode with a mesh screen. To introduce ions into the accelerator, the repeller electrode must be held at ground potential. Although we used DC potentials for the ion-focusing optics, the grounded mesh screen suppressed the penetration of disturbing stray electric fields into the accelerator. Under these conditions, the ions could enter the accelerator and reach the acceleration region, where they were accelerated by a pulsed electric field. We also developed two high-voltage pulse generators: one generated high-voltage pulses of up to 20 kV with a fast rise time of 90 ns, and the other provided high-voltage pulses of up to 7 kV with a rise time of 50 ns. These generators have a high fidelity and a small jitter. Under these conditions, the influence of factor (d) can be suppressed to a negligible level.

To reduce the effect of factor (c), one should use high-voltage power supplies with a high stability. We used commercially available power supplies with a nominal stability of 0.005%, including temporal drift and ripple. We used six power supplies (one for the pulsed acceleration system, three for the ion-focusing optics, and two for the reflector). Including the fidelity of the pulsed acceleration field, we estimated a total stability of about 0.013% (\( (7 \times 0.005)^{1/2} \)), equivalent to a mass resolution limit of about 7700. Note that this limiting value cannot be reduced, even if the flight length is increased on longer TOF mass spectrometers.

For the ion detection system, we used a fast-response microchannel-plate detector with a detection diameter of 14.5 mm (Hamamatsu P4655). For the data-recording system, we used a digital oscilloscope with a bandwidth of 2 GHz or a digital multistop time digitizer with a 0.25-ns resolution (FAST ComTec P7887). Although the current-detection mode, where the ion signal is measured by accumulating the waveforms of the individual ion currents on the oscilloscope, was useful for qualitatively measuring the relative abundance of ions, the pulse-counting method by the multistop time digitizer enabled us to attain a wide dynamic range and sufficient ion count accuracy for quantitative measurement of the TOF spectrum. In the pulse-counting method, the intensity of the ion signal (the ion flux) should be reduced to a sufficiently low level so that multiple ions of identical mass do not hit the detector simultaneously. Mass measurements in this work were obtained by the pulse-counting method.

On the basis of basic considerations, we have constructed a reflector TOF mass spectrometer that was designed to fit within an 80-cm-long vacuum chamber. The design parameters of the TOF mass spectrometer are listed in Table 1.

Because factors (a)–(e) introduce their corresponding time resolutions, \( \Delta t_i \) (\( i = a, b, c, d, e \)), the effective total time resolution \( \Delta t \) is approximately given by:

\[
\Delta t = \left( \sum (\Delta t_i)^2 \right)^{1/2}
\]

The mass resolution \( R \) is sensitively dominated by the largest time resolution \( \Delta t_i \). The mass resolution of small-mass ions is mainly determined by factor (e) and the jitter (factor (d)) because small-mass ions have short \( t_{TOF} \) values. Lower acceleration potentials \( U_a \) (lower kinetic energies \( K_a \)) lead to higher mass resolution for small-mass ions but lower detection efficiency for large-mass ions. We typically used an acceleration potential of \( U_a = 10 \) kV in normal measurements. Mass measurements with the higher acceleration potentials attain higher detection efficiencies and a wider mass range but lower mass resolution for small-mass ions.

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**Figure 2.** Schematic view of a TOF mass spectrometer with a one-stage accelerator and a two-stage reflector.
A low mass cut-off filter by the pulsed acceleration

A pulsed acceleration method is widely used for TOFMS. Although the pulse shape should be an ideal step function, a generated pulse shape has a finite rise-time. Here, we briefly mention the influence of a finite rise-time and show that finite rise-time can function as a low mass cut-off filter in the IA-TOF system.

To simplify the notation, we assume that ions with no initial velocity are at $P_0$ (see Fig. 2), and then they are accelerated by the pulsed acceleration field. The acceleration voltage $U_a(t)$ is given by:

$$ U_a(t) = \begin{cases} 0 & t \leq 0 \\ U_0 & 0 \leq t \leq t_r \\ U_0 & t \geq t_r \end{cases} $$(5)

where $t_r$ is the rise time and $U_0$ is a steady acceleration voltage. The potential energy of ions in the accelerator is converted into kinetic energy $E(m)$. We define $E_0$ and $m_r$ as follows:

$$ E_0 = eU_0 \frac{s}{r_a} $$

$$ m_r = \frac{E_0 t_r^2}{6} $$

where $E_0$ is the kinetic energy at the point where $m = m_r$.

Relative Intensity (%) 

$$ E(m) = E_0 \left(1 - \frac{m_r}{4m}\right) \quad (m \geq m_r) $$

As $m$ decreases, $E(m)$ approaches $E_0$. Ions with lower mass obviously have lower $E(m)$ and cannot reach the detector, because of their irregular flight through the orthogonal accelerator, the ion-focusing optics, and the reflector.

In our IA-TOF system, we estimate that ions with $m > 48.2$ u have enough kinetic energy to be mass-measured with a high mass resolution. The pulse acceleration also acts as a low mass cut-off filter to cut off the signals of the Li$^+$ ions.

RESULTS AND DISCUSSION

Fragment-free ionization and high mass resolution

To evaluate the performance of our IA-TOF system in analyzing gas-phase organic compounds in ambient air, we analyzed a benzene ($C_6H_6$) sample diluted with $N_2$ gas at atmospheric pressure. A $C_6H_6$ sample at a partial pressure of 0.002% was prepared in a gas bottle and introduced into the IA ion source through a mass flow controller. The gas flow rate was 4 sccm (standard cubic centimeters per minute), and the pressure in the IA ion source was kept at 100 Pa. For comparison, we also analyzed the same sample with a conventional EI-QMS system.

Figure 3 shows a typical spectrum recorded by EI-QMS of a $C_6H_6$ sample. EI dissociates the benzene molecules and produces a variety of fragment ions. If any contaminants appear in the mass spectrum, distinguishing them from the benzene fragment ions is generally very difficult. Therefore, when a sample is a complex mixture of compounds, a minimum observable mass $m_o = 3.5 m_r$, and the other is the minimum mass that can be measured with a high mass resolution, $m_b = 12.5 m_r$.

Although the restriction of the minimum observable mass is a disadvantage of TOFMS with a single-stage accelerator and a high-voltage acceleration pulse, the restriction becomes an advantage of our IA-TOF setup because it acts as a low mass cut-off filter.

In the IA ionization method, there are Li$^+$ ions that are not consumed by the formation of [M+Li]$^+$ adduct ions. The excess Li$^+$ ions in TOF measurements interfere with the detector system by producing ringing of the ion signal, saturation and destruction of the amplifying system, and background noise.

By means of pulsed acceleration with $U_0 = 10$ kV and $t_r = 90$ ns, we obtain $m_o = 13.5$ u and $m_b = 48.2$ u. The ions with $m > 48.2$ u have enough kinetic energy to be mass-measured with a high mass resolution. The pulse acceleration also acts as a low mass cut-off filter to cut off the signals of the Li$^+$ ions.

Table 1. Design parameters of the TOF-MS system. $L_{eff}$ is the effective flight length that the ions travel at the constant drift velocity corresponding to the kinetic energy $K_0$ during their flight time $t_{TOF}$. Refer to Fig. 2 for notation of other parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_a$</td>
<td>15 mm</td>
<td></td>
</tr>
<tr>
<td>$s$</td>
<td>10 mm</td>
<td></td>
</tr>
<tr>
<td>$L_{d1}$</td>
<td>550 mm</td>
<td>Saturation</td>
</tr>
<tr>
<td>$L_{d2}$</td>
<td>480 mm</td>
<td></td>
</tr>
<tr>
<td>$l_b$</td>
<td>48 mm</td>
<td></td>
</tr>
<tr>
<td>$L_c$</td>
<td>60 mm</td>
<td></td>
</tr>
<tr>
<td>$L_r$</td>
<td>43.41 mm</td>
<td></td>
</tr>
<tr>
<td>$L_{eff}$</td>
<td>673 mm</td>
<td>effective flight length</td>
</tr>
<tr>
<td>$K_0$</td>
<td>13.33 (6.667) keV</td>
<td>kinetic energy</td>
</tr>
<tr>
<td>$U_0$</td>
<td>13.33 (6.667) kV</td>
<td>potential at $P_0$</td>
</tr>
<tr>
<td>$U_{b}$</td>
<td>20 (10) kV</td>
<td></td>
</tr>
<tr>
<td>$U_{c}$</td>
<td>9.782 (4.891) kV</td>
<td></td>
</tr>
<tr>
<td>$U_{r}$</td>
<td>4.938 (2.469) kV</td>
<td></td>
</tr>
</tbody>
</table>

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The detected counts of the various molecular ions are consistent with the values theoretically expected from the natural isotope abundance of \([\text{C}_6\text{H}_6+\text{Li}]\).

By using mass spectrometry with a sufficiently high mass resolution, one can distinguish isobaric ions that have the same nominal mass but different exact masses. Butane \((\text{C}_4\text{H}_10)\) and acetone \((\text{C}_3\text{H}_6\text{O})\) are typical examples of volatile organic compounds. They have the same nominal mass of 58 u, but the exact mass difference between them is 58.094–58.058 = 0.036 u. The lowest mass resolution to distinguish their adduct ions, \([\text{M}+7\text{Li}]^+\), is therefore \((58 + 7)/0.036 = 1800\). Thus, distinguishing their ions is easy with the present IA-TOF system. High-resolution mass measurements can help in identifying the empirical formula of a molecule.

In the experiment, we purposely did not exclude water contamination from the system. Moisture makes up approximately 0–2% of the earth’s atmosphere. If there is water contamination, the \(\text{Li}^+\) ions are captured by the water molecules. In addition, \([\text{H}_2\text{O}+\text{Li}]^+\) ions have a small \(m/z\) value (25) and can attach to molecules \(\text{M}\) to yield cluster ions \([\text{H}_2\text{O}+\text{M}+\text{Li}]^+\). This is one of the reasons that \([\text{H}_2\text{O}_2+\text{Li}]^+\) and \([\text{H}_2\text{O}+\text{C}_6\text{H}_6+\text{Li}]^+\) ions were observed in the spectrum shown in Fig. 4. Careful sample preparation is necessary for measurement of samples containing water.

Preliminary results obtained by IA-QMS show that the cluster ions are not observed and that the intensity of the adduct ion signal is directly proportional to sample concentration when the sample concentration is below 0.1%. The IA technique is applicable to quantitative analysis in this concentration range.

Wide mass range and high mass accuracy

In TOF measurements, we obtain only a time value for each signal, \(t\). In a TOF mass spectrometer with an effective flight length of \(L_{\text{eff}}\) the time-of-flight \(t_{\text{TOF}}\) is given by:

\[
t_{\text{TOF}} = L_{\text{eff}} \left( \frac{m}{2ZU_0} \right)^{1/2}
\]

for an ion of mass \(m\), charge \(z\), and acceleration potential \(U_0\).

Then \(m/z\) is represented in the general form:

\[
m/z = C_1(t - C_2)^2
\]

where \(C_1\) and \(C_2\) are parameters determined by experimental conditions such as those listed in Table 1. However, in practice, \(C_1\) and \(C_2\) are fitted by calibration experiments using mass marker molecules.

Equation (10) is valid for all masses as long as the acceleration potential \(U_0\) is kept constant during the period of ion acceleration. Because our high-voltage pulse generators can generate high-voltage rectangular pulses with fast rise times, Eqn. (10) can be applied over a wide mass range even in the pulsed acceleration method.

To determine the conversion parameters \(C_1\) and \(C_2\) and demonstrate the versatility of our system over a wide mass range, we obtained the mass spectrum of the mass marker Ultrimark 1621 (Lancaster Synthesis). Ultrimark 1621 is a mixture of fluorinated phosphazenes of the formula \(\text{C}_{18}\text{H}_{36}\text{O}_{32}\text{P}_{30}\text{F}_{36}\) (\(m\): 921 + 100\(n\), where \(n = 0–12\)). A direct inlet probe (DIP) with a heater was
employed to evolve the liquid sample. A small amount of sample was smeared on the head of the DIP and vaporized in the IA ion source at a surrounding N2 gas pressure of 100 Pa.

Figure 5 shows the mass spectrum of Ultramark 1621. Ions over a wide mass range up to \( m/z \) 3400 are clearly observed. Ions of \( m/z < 350 \) are due to traces of residual styrene monomers, dimers, and trimers from pyrolysis of polystyrene samples (see later; Fig. 6).

We adopted two reference time peaks to obtain the conversion parameters in Eqn. (6). One was the time peak at \( m/z \) 111.079, corresponding to the styrene monomer \( ^{12}\text{C}_8\text{H}_8\text{Li}^+ \), and the other was the peak at \( m/z \) 1628, corresponding to Ultramark 1621. By using Eqn. (10) with the fitted conversion parameters, we obtained the calibrated mass spectrum shown in Fig. 5.

In the positive-ion electrospray ionization mass spectrum of Ultramark 1621, where the peaks correspond to \([\text{M}+\text{H}]^+\), the dominant peaks appeared from \( m/z \) 922 to 2122 at a

![Figure 5. Typical mass spectrum of the mass marker Ultramark 1621. Compounds over a wide mass range up to \( m/z \) 3400 are clearly mass-analyzed with high mass accuracy.](image)

![Counts / 5 min vs. m/z for different temperatures](image)

**Figure 6.** Typical mass spectra of the pyrolysis products of polystyrene samples. Pyrolysis products over a wide mass range are clearly mass-analyzed. IA-TOF realizes on-line and real-time measurements of temporally evolving processes.
regular interval of 100 m/z.\(^{15}\) Because the peaks in the IA-TOF mass spectrum correspond to [M+Li]\(^+\), the dominant peaks appeared from \(m/z\) 928 to 1828 at a regular interval of 100 m/z (Fig. 5). Mass accuracy is defined as the difference between the measured mass and the exact mass. The obtainable mass accuracy, \(\Delta m/z\), was determined to be less than 0.02\% from the locations of the various mass peaks between \(m/z\) 928 and 1828. The mass accuracy was dominated by the mass resolution of about 5000.

Additional peaks appear in the spectrum of Fig. 5 in the mass range between 2000 and 3400. High-accuracy mass measurements enabled us to identify these peaks. The dominant peaks are located from \(m/z\) 2049 to 3249 at a regular interval of 100 m/z. These peaks are due to clustering of ions with \(m\) values from \(m\) 921 to 921. For example, the peaks at \(m/z\) 2849 are due to clustered species with masses such as \((921+1921+7)\), \((1021+1821+7)\), \ldots, \((1,321+1,521+7)\), and \((2 \times 1421+7)\). This fact verifies that Eqn. (6) is valid over a wide mass range up to \(m/z\) 3400. Thus, we have demonstrated that our IA-TOF system has a high mass accuracy over a wide mass range.

**Real-time measurements over a wide mass range**

We also evaluated the performance of the IA-TOF system by analyzing samples originally in the solid phase. Characterization of the gases produced during heating and firing processes is important to understand their toxicity or reaction mechanisms. Such characterization is also widely applied in the mass spectral analysis of synthetic polymers. Here we report the mass spectral analysis of the pyrolysis products of polystyrene briefly.

We used a small piece of polystyrene (~0.03 mg) as a sample. The sample in a micro-vial was placed on the head of the DIP and directly introduced into the IA ion source. The DIP had a heater and a thermocouple. The sample was heated under programmed control in the ion source at a surrounding \(N_2\) gas pressure of 100 Pa. The heating rate was \(10^8\) C min\(^{-1}\). Each mass spectrum was accumulated for 5 min at a TOF sweep of 300 Hz.

Figure 6 shows mass spectra of the pyrolysis products of the polystyrene samples for various temperature ranges. Note that signal height is plotted on a logarithmic scale. Pyrolysis products over a wide mass range are clearly mass-analyzed. The detailed mass spectroscopy of the pyrolysis of the polystyrene samples will be reported elsewhere. Briefly, the dominant ions initially observed in the mass spectrum (Fig. 6a) are adduct ions corresponding to styrene monomers [(St)\(_1\)], styrene dimers [(St)\(_2\)], and styrene trimers [(St)\(_3\)]. With increasing temperature, the [(St)\(_1\)], [(St)\(_2\)], and [(St)\(_3\)] signals increase, and signals corresponding to larger styrene clusters appear (Fig. 6b). At \(T = 400–450\) C, signals corresponding to styrene clusters, [(St)\(_n\)], up to \(n = 10\), and their degraded products are observed (Fig. 6c). At the end of the measurement (Fig. 6d), the signal levels decrease because the sample source material is exhausted.

Pyrolysis/GC (Py/GC) and GC/EI-MS systems are widely used to study the pyrolysis of polymers, but previous studies on the pyrolysis of polystyrene have been able to identify only dominant small-size components such as styrene monomers, dimers, and trimers.\(^{16}\) In general, real-time and on-line measurements over a wide mass range have been impractical. In marked contrast, IA-TOF enables us to measure mass spectra over a wide mass range in real time. The wide dynamic range and high signal-to-noise ratio of IA-TOF allow us to measure minor components such as large styrene clusters, [(St)\(_n\)], up to \(n = 10\). In addition, whereas discerning the thermal process from fragments in the EI spectra is difficult, IA-TOF enables us to understand the detailed thermal process owing to fragment-free ionization. Therefore, IA-TOF is suitable for detailed analysis of the thermal properties and vaporization process of chemical materials.

The mass spectra in Fig. 6 were accumulated for 5 min to realize a wide dynamic ion-counting range. We used a heating rate of 108 C min\(^{-1}\), but much faster heating rates are possible. The response time of the IA ion source is about 10 s to substitute the resident gas for new gas. Mass measurements of only dominant ions require an accumulation time of only a few tens of seconds by TOF-MS. Thus, IA-TOF is suitable for on-line and real-time measurements of temporally evolving processes.

Although high mass resolution measurements can help in identifying the empirical formulas of molecules, fragment-free ionization provides essentially only molecular mass information. Tandem mass spectrometry (MS/MS) is one solution for overcoming this problem. A higher level of performance will be achieved by combining an IA-TOF system (MS-1) with a laser MS (MS-2).

**CONCLUSIONS**

We have developed a tabletop IA-TOF system and evaluated its performance by analyzing specimens originally in the gas, liquid, and solid phases.

For benzene diluted with \(N_2\) gas at atmospheric pressure, we obtained fragment-free mass spectra with a high mass resolution of 4700. Fragment-free ionization allows direct mass measurements of organic samples in complex mixtures without pre-separation. By using a sufficiently high mass resolution, one can distinguish ions with the same nominal mass but different exact masses and identify the empirical formula of a molecule.

We also analyzed samples originally in the liquid and solid phases by using a direct inlet probe with a heater. Using the Ultramark 1621 mass marker, we demonstrated that our IA-TOF system has a high mass accuracy, \(\Delta m/z <0.02\%\), over a wide mass range. The mass accuracy was dominated by the mass resolution. In measurements of the temporal evolution of the pyrolysis products of polystyrene samples, we observed that the types and amounts of pyrolysis products depended on temperature.

Our IA-TOF system is capable of measuring mass spectra over a wide mass range in real time, and its wide dynamic range and high signal-to-noise ratio allow measurement of not only dominant components, but also minor components. These results show that the IA-TOF system is a versatile scheme for the real-time analysis of molecules over a wide mass range with a high mass resolution and a high mass accuracy.
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