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Citation	Journal of Mass Spectrometry, 57(11), e4892 https://doi.org/10.1002/jms.4892
Issue Date	2022-11-22
Doc URL	http://hdl.handle.net/2115/90847
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Type	article (author version)
File Information	J. Mass Spectrom._57(11)_e4892.pdf



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Development of electrostatic-induced charge detector for multiturn time-of-flight mass spectrometer

Short title

Development of non-destructive ion detector for multiturn TOF-MS

Ken-ichi Bajo^{1*}, Jun Aoki^{2,3,4}, Morio Ishihara², Shizuho Furuya⁵, Masahiro Nishimura⁵, Miwa Yoshitake⁵ and Hisayoshi Yurimoto^{1,5}

¹ Department of Earth and Planetary Sciences, Hokkaido University, Sapporo, Japan

² Department of Physics, Graduate School of Science, Osaka University, Toyonaka, Japan

³ Graduate School of Frontier Biosciences, Osaka University, Suita, Japan

⁴ Riken Center for Biosystems Dynamics Research, Kobe, Japan

⁵ ISAS/JAXA, Sagamihara, Japan

* Corresponding author. E-mail: k-bajo@eis.hokudai.ac.jp Tel.: +81 11 706 9174.

Keywords: multiturn TOF-MS, electrostatic-induced charge detector, MULTUM, non-destructive ion detection, mass assignment

1 Abstract

2 We developed an autocorrelation function to resolve the overtaking problem in
3 a multiturn time-of-flight mass spectrometer (TOF-MS). The function analyzes the
4 characteristic period for one lap of each ion packet and derives a mass spectrum from a
5 signal pulse train composed of multiturn ion packets. To detect the ion pulse train, a new
6 non-destructive ion detector was developed and installed in the multiturn orbit of
7 MULTUM-S II. This detector is composed of an electrostatically induced charge detector,
8 a preamplifier, and a digitizer. The electrostatic noises are smaller than the single-ion
9 signals owing to the accumulation of the multiturn TOF spectrum. The conventional ion
10 detector of TOF-MS is operated after collecting the signal pulse train. The multiturn TOF
11 spectrum was convolved with an autocorrelation function to derive the mass spectrum.
12 The convolved mass spectrum performed a mass resolving power (MRP) of 28,200 at m/z
13 69 and mass accuracy of 28 ppm for the perfluorotributylamine (PFTBA) gas sample.
14

15 **1. Introduction**

16 Multiturn ion optics with perfect space and time focusing were developed to
17 achieve infinite mass resolving power (MRP) time-of-flight mass spectrometry.¹ The
18 optics were installed in time-of-flight mass spectrometers (TOF-MS), MULTUM, and
19 MULTUM II, which provide ultra-high MRP to attain an $M/\Delta M = 6 \times 10^5$.²⁻⁸ The optics
20 also dramatically reduce the size of TOF-MS.

21 Although the optics provided ultra-high MRP with a compact MS, it introduced
22 the so-called overtaking problem for the mass spectrum, in which ions having small m/z
23 overtake ions having large m/z when the flight time (pass length) is increased.⁹ As a result,
24 the time-of-flight (TOF) spectrum after the flight is not aligned according to m/z . When
25 many ion species with different m/z simultaneously fly in the multiturn trajectory, the
26 overtaking ions complicate the TOF spectrum. This characteristic makes the universal use
27 of multiturn TOF-MS difficult, and the applications may be restricted to a narrow range
28 of m/z in the multiturn trajectory.^{10,11} In this study, we traced every multiturn ion using a
29 novel electrostatic-induced charge detector (iCD) installed in multiturn optics. We
30 analyzed the overtaking problem of the multiturn TOF spectrum using an autocorrelation
31 function to derive the mass spectrum.

33 **2. Electrostatic-induced charge detector (iCD)**

34 An electron impact (EI) type TOF-MS, infiTOF (MSI. TOKYO, Inc., Japan),
35 equipped with MULTUM-S II was used.^{9,12} An iCD was installed in the ion optics of the
36 MULTUM-S II (Figure 1a).

37 A stainless steel tube with an inner diameter of 6 mm and a length of 18 mm was
38 used to make the iCD. The iCD connects the input gate electrode of a field-effect
39 transistor to a charge-sensitive preamplifier (CSA) A250CF CoolFET® (Amptek Inc.,
40 USA) (Figure 1b). The iCD is shielded by an exterior body at ground potential. The iCD
41 was set in the multiturn ion optics between the electrostatic sectors of the MULTUM-S II
42 (Figure 1a). The electrostatic-induced charges caused by a multiturn ion packet were
43 detected by the iCD. When an ion packet with positive charges (+Q) passes through the
44 iCD, charges -Q and +Q are induced on the inner and outer surfaces of the iCD,
45 respectively. The +Q charges can be measured using CSA without any effect on the ion
46 packet (Figure 1b). The output voltage is 0.64 μV when a single charged ion passes
47 through the iCD.

49 **3. Data acquisition system**

50 A schematic illustrating the data acquisition system for the electrostatic-induced

51 charge detection is shown in Figure 2. This system resembles that of the data acquisition
52 system reported by Bajo et al.¹³ The pulse signals from the A250CF preamplifier are
53 converted into 10-bits digital signals using the NI PXIe-5160 (5160) digitizer. The
54 sampling rate and voltage resolution are 104.167×10^6 samples s^{-1} and $48.8 \mu V$ (10-bits
55 and $\pm 0.025V$ for peak-to-peak voltage), respectively. Streaming data processing and
56 recording are performed using the NI PXIe-8880 (8880) as a controller of the PXI-
57 platform (National Instruments corp., USA). This system is controlled using the
58 LabVIEW program.

59 The 10-bits digital signals are converted into 16-bits iCD spectrum, and then
60 multiplied and subtracted by the gain and the offset of 5160 digitizer settings, respectively.
61 The arbitrary repetitive acquisition data for the iCD spectra are converted into 64-bits
62 double precision floating point numbers and averaged. The acquisition data are stored in
63 the 8880. A master-trigger of 1 V rectangle pulse from the infiTOF is used and introduced
64 to a digital delay/pulse generator (Model 575, Berkeley Nucleonics Corporation, USA).
65 The Model 575 converts to a transistor-transistor-logic pulse from the master-trigger and
66 outputs to the digital multimeter NI PXIe-6361. Trigger synchronization among the
67 converted master-trigger and PXI modules is performed using real-time system
68 integration in the backplane of the NI PXIe-1082 chassis.

69 The noise characteristics of the iCD system are evaluated by a blank spectrum,
70 which is produced by the same data acquisition procedure as the normal infiTOF
71 operation⁹ without the extraction of ions from the EI source. The baseline of the iCD
72 spectrum is modulated by switching pulse noises derived from the rising and falling
73 voltages of the entrance and exit deflection electric sectors of MULTUM-S II (Figure 3).
74 To remove the modulation, a ± 48 ns moving average was applied to the blank iCD
75 spectrum. The moving average was repeated 20 times. The moving average spectrum was
76 subtracted from the blank iCD spectrum. The standard deviations of the noise signals
77 decrease theoretically with increasing accumulation of the blank iCD spectrum with a
78 slope to the power of ~ -0.5 (Figure 4). For an iCD spectrum, the estimated noise signal
79 is 1000 ions, while for iCD spectra obtained after 10^8 accumulations, the estimated noise
80 signal is ~ 0.3 . This indicates that after 10^8 accumulations, single-ion detection with three
81 standard deviation reliability is obtained. Thus, a dynamic range of this system is
82 estimated to $\sim 3 \times 10^4$ because $\sim 10^4$ ions from the ion source can be extracted for single
83 mass scan and the minimum noise level is ~ 0.3 ion.

84

85 **4. Experimental method**

86 N_2 and perfluorotributylamine (PFTBA, molecular weight: 671) gases are used.

87 N₂ gas is introduced into the EI ion source of the infiTOF with He as the carrier gas. In
88 the case of PFTBA, the vaporized gas is directly introduced into the ion source. The
89 pressure in the ionization chamber is set to $\sim 1 \times 10^{-2}$ Pa during the measurements. The
90 ion packet produced in the ion source is introduced into the ion trajectory of the
91 MULTUM-S II using an entrance electric sector (Figure 1a). The voltage of the entrance
92 electric sector drops to the ground potential before the ions return to the sector. The signals
93 from ion packets during multiturning are detected by the iCD system. After multiturning,
94 the ion packets are output using an exit electric sector and detected by an electron
95 multiplier (EM) (148006 Fast-TOF Plus, ETP Ion Detect Pty Ltd., Australia).

96

97 **5. Data reduction procedure**

98 **5.1. Baseline correction**

99 Figure 5 shows the iCD spectrum of the N₂–He gas mixture measured 2.4×10^6
100 times and averaged. Random noise levels of the accumulated spectrum correspond to 0.61
101 μ V or 0.95 ions as standard deviation (Figure 4).

102 The baseline of the iCD spectrum is modulated by the entrance pulses, as
103 discussed in Section 3 (Figure 5). The modulations of the baseline are removed in the
104 following steps: (1) selecting ion signals from the iCD spectrum using a differential filter
105 (Figures 6a₁, 6a₂, and 6b). Absolute ion intensities larger than the noise level in Figure 6b
106 are defined as peaks of ion signals. The standard deviation described above (0.95 ions)
107 was used as the noise level. Each peak of ion signals is defined as ± 58 ns outward from
108 the boundary between the peak profile and the noise level. The time width is determined
109 by the peak widths of several high peak profiles. The ion and noise signals are shown in
110 yellow and black, respectively (Figure 6c). (2) Ion signals from the differential iCD
111 spectrum are removed from the iCD spectrum. The removed areas are interpolated
112 linearly between both ends of the remaining data (Figure 6d). (3) To obtain the modulated
113 baseline profile, a ± 48 ns moving average is applied to the interpolated spectrum 20 times
114 (Figure 6e as a baseline profile of Figure 6a₂). (4) The baseline profile is subtracted from
115 the iCD spectrum (Figures 6f₁ and 6f₂). The baseline-corrected iCD spectrum is shown in
116 Figure 7.

117

118 **5.2. Convolution of iCD mass spectrum with autocorrelation function**

119 An ion packet of m/z periodically passes through the iCD with a lap time of τ .
120 The autocorrelation function shown below converts the baseline-corrected iCD spectrum
121 into a mass spectrum: A function $f(\tau, t)$ that defines the ion packet $C(\tau)$ is denoted as the
122 conditional series sum of $Q(i\tau)$, which is the charge of an ion packet for each lap.

123
$$f(\tau, t) = \sum Q(\tau, t) g(\tau, t) = \sum_{i=1}^n Q(i\tau, t) \frac{1}{n} \quad (1)$$

124 where t is a variable of TOF, and i is the multiturn number.

125 At time $t = t_a$,

126
$$g(\tau, t) = \begin{cases} 0 & (Q(i\tau, t_a) < -V_{dis}) \\ 1 & (Q(i\tau, t_a) \geq -V_{dis}) \end{cases} \quad (2)$$

127 where V_{dis} , discrimination voltage between peaks and noise, is based on the noise level of
 128 the iCD spectrum. This operation removes noise signals from the iCD spectrum. The
 129 standard deviation of the noise of the measurement condition was set at $V_{dis} = 0.6 \mu\text{V}$.
 130 Furthermore, we set $Q((i+1)\tau, t_a) = Q(i\tau, t_a)$ if $Q((i+1)\tau, t_a)$ is greater than $Q(i\tau, t_a)$.
 131 This operation removes the contribution of the overlapping ion peaks in the iCD spectrum.
 132 Then, $C(\tau)$ can be expressed by the following equation:

133
$$C(\tau) = \int f(\tau, t) dt \quad (3)$$

134 Expanding this expression, we get the following equation:

135
$$C(\tau) = \int_{-\Delta t}^{\Delta t} \frac{1}{n} \{Q(\tau + t_0 + t) + Q(2\tau + t_0 + t) + \dots + Q(n\tau + t_0 + t)\} dt \quad (4)$$

136 where t_0 is the TOF of the ion packet from the exit slit of the ion source to the iCD, which
 137 is proportional to τ depending on the m/z , i.e., $t_0 = 0.3781 \tau$. The coefficient 0.3781 is a
 138 unique constant for the MULTUM-S II. Δt is the value that complements to t_0 . We set Δt
 139 = 288 ns, which is nearly twice the peak width of the iCD spectrum (Figure 7b). A larger
 140 Δt provides a higher redundancy for the calculation but are computationally expensive.

141 A convolution from the iCD spectrum to the mass spectrum is calculated as $C(\tau)$
 142 over a range of τ_{min} to τ_{max} in s_τ increments. The τ_{min} and τ_{max} are determined from the
 143 mass spectrum obtained using MULTUM-S II operated in the half-cycle mode.⁹ The s_τ
 144 corresponds to the resolution of the m/z axis. We set $s_\tau = 0.5$ ns to derive a mass spectrum
 145 of appropriate mass resolution. The m/z is calculated from τ if we use one or more internal
 146 mass references.

147 Figure 8 shows the mass spectrum of the N₂–He gas mixture convolved using
 148 Equation (4) from the iCD spectrum, as shown in Figure 7a. The m/z is calculated using
 149 the ⁴He and ²⁸N₂ signals as internal mass references. The largest ion intensity among the
 150 ions is in the mass spectrum with ²⁸N₂⁺ as the sample gas, and the second largest is in the
 151 spectrum with ⁴He⁺ as the carrier gas. We observed ¹⁴N¹⁵N⁺ of the N₂ isotopologue and
 152 ¹⁴N⁺ as fragment ion of N₂. Peaks of H₂¹⁶O⁺, ³²O₂⁺, and ⁴⁰Ar⁺ were also detected, which
 153 were from the residual air in the ion source.

154

155 **5.3. Mass resolving power of the convolved mass spectrum**

156 Given an ion packet at i laps of the iCD spectrum, the MRP of the ion packet
 157 peak, MRP_{iCD} is calculated as:

$$158 \quad MRP_{iCD}(i) = \frac{i\tau}{2\Delta T_i} = \frac{iL}{2l_{iCD}} \quad (5)$$

159 where ΔT_i is the full half-width maximum of the ion peak at i laps, L is the flight pass
 160 length for one lap, and l_{iCD} is the length of the iCD tube. The L and l_{iCD} for MULTUM-S
 161 II are 0.65 m and 0.018 m, respectively.

162 According to Equation (5), the MRP_{iCD} of N_2^+ increases linearly with increasing
 163 i (Figure 9). The MRP of the convolved mass spectrum, MRP_{conv} calculated from Figure
 164 8 also increases linearly with increasing i , but the slope is one-third of the slope of MRP_{iCD}
 165 because of averaging the iCD N_2 peaks. This indicates that the MRP performance
 166 improves if we combine the convolved mass spectrum and ion peaks extracted from the
 167 iCD spectrum.

168

169 **6. Extended convolution using iCD and multiturn TOF spectra (Extended convolved** 170 **mass spectrum)**

171 To overcome the lower MRP performance of the convolved mass spectrum, we
 172 applied a combination analysis between the iCD and the conventional EM ion detector.
 173 Therefore, we used the experimental results of PFTBA because the characteristics of the
 174 mass spectrum of PFTBA have been well studied and widely used for the mass calibration
 175 of EI mass spectrometry.¹⁴

176 The multiturn TOF spectrum of PFTBA measured using the EM detector is
 177 shown in Figure 10. The convolved mass spectrum calculated from the simultaneously
 178 measured iCD spectrum is shown in Figure 11. In this calculation, we set $V_{dis} = 0$ V instead
 179 of 0.6 μ V to reject small ion signals close to noises.

180 We combined the convolved mass spectrum and multiturn TOF spectrum to
 181 formulate an extended convolved mass spectrum. To replace the peaks of the convolved
 182 mass spectrum with the peaks of the multiturn TOF spectrum, Equation (4) is changed to:

$$183 \quad C(t) = I_{EM}(n\tau + t_0 + t_{ex}) \quad (6)$$

184 where I_{EM} is the ion intensity of the multiturn TOF spectrum at $(n\tau + t_0 + t_{ex})$. t_{ex} is the
 185 TOF from the iCD to the EM detector to extract from the multiturn trajectory and is given
 186 as:

$$187 \quad t_{ex}(m/z) = t_a(m/z)^{1/2} + t_b \quad (7)$$

188 where t_a and t_b are constants given by the MS conditions (acceleration, toroidal sector
 189 electric fields, and MATSUDA plate voltages). In this study, we determined t_a and t_b using
 190 internal mass references at m/z 68.9952 (CF_3^+) and 218.9856 ($C_4F_9^+$). Using Equation (6),

211 we replaced the peaks appearing in Figure 11 with those appearing in Figure 10 to
 212 construct an extended convolved mass spectrum of PFTBA (Figure 12). We compared the
 213 peaks at m/z 130.9920 ($C_3F_5^+$) in the mass spectra (Figure 13). The MRP of the extended
 214 convolved mass spectrum is the fully performed multiturn ion trajectory of the
 215 MULTUM-S II.

216 The TOF of a peak of ion x on the multiturn TOF spectrum, T_x is expressed as:

$$217 \quad T_x = \frac{n_x L + l}{v_x} \quad (8)$$

218 where n_x is the number of multiturn laps of ion x at extraction, l is the flight pass length
 219 for half-cycle mode operation, and v_x is the flight speed of ion x. The flight pass lengths
 220 are independent of ion x. From the peaks of ions x and y, we get:

$$221 \quad \frac{v_x}{v_y} = \sqrt{\frac{m_y}{m_x}} \quad (9)$$

222 where m_i and m_j are the masses of the ions x and y, respectively. Then, L and l are
 223 expressed as:

$$224 \quad L = \frac{T_x v_x - T_y v_y}{n_x - n_y} = \frac{T_x - T_y \sqrt{\frac{m_x}{m_y}}}{n_x - n_y} v_x = \tau_x v_x \quad (10)$$

$$225 \quad l = v_x (T_x - n_x \tau_x) \quad (11)$$

226 where τ_x is the lap time of ion x. Therefore, if ions x and y are used as internal references,
 227 the T_z for ion z is calculated as:

$$228 \quad T_z = (\tau_x (n_z - n_x) + T_x) \sqrt{\frac{m_z}{m_x}} \quad (12)$$

$$229 \quad m_z = m_x T_z^2 (\tau_x (n_z - n_x) + T_x)^{-2}. \quad (13)$$

230 The measured masses m_z on the extended convolved mass spectrum were calculated from
 231 Equation (13) using two internal mass reference peaks of CF_3^+ and $C_4F_9^+$. The molecular
 232 formulas, exact masses, measured masses, mass differences, mass accuracies, number of
 233 laps, and MRPs for PFTBA fragment ions are summarized in Table 1. The mass
 234 accuracies are less than 80 ppm. The root mean square of the mass accuracies of the
 235 system is 28 ppm. The value 28 ppm corresponds to the modulation amplitude of the
 236 power supply because modulation causes fractionations of the lap time of ions by voltage
 237 modulations of the electric sectors.⁸

238

239 7. Conclusions

240 We developed an iCD system to obtain mass spectra in a non-destructive mode.
 241 We also formulated an autocorrelation function for this system to resolve the overtaking
 242 problem in the multiturn TOF-MS. The iCD system provides m/z assignments of flying

223 ions along the multiturn trajectory. A mass spectrum was constructed from the iCD
224 spectra. An MRP of up to ~30,000 and mass accuracy of tens of ppm have been realized
225 by the iCD system installed in the MSI infiTOF.
226

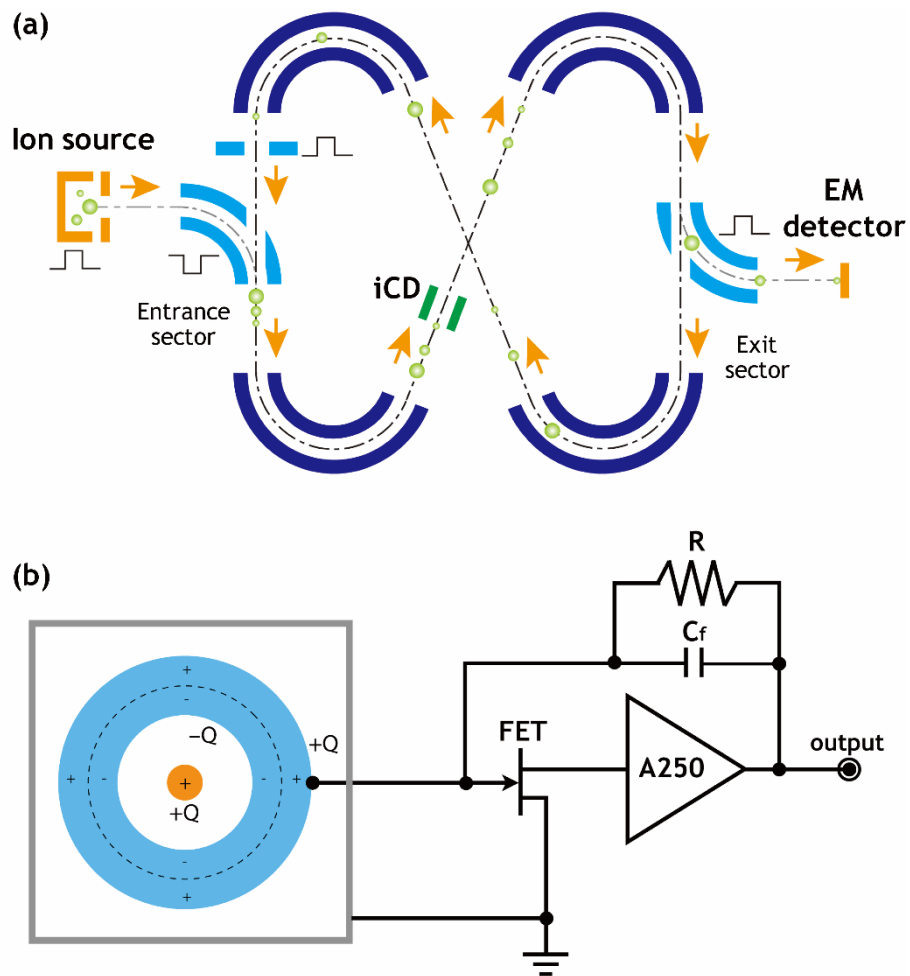
227 Acknowledgements

228 We thank the anonymous reviewer for the constructive comments. We would
229 like to thank Editage (www.editage.com) for English language editing.

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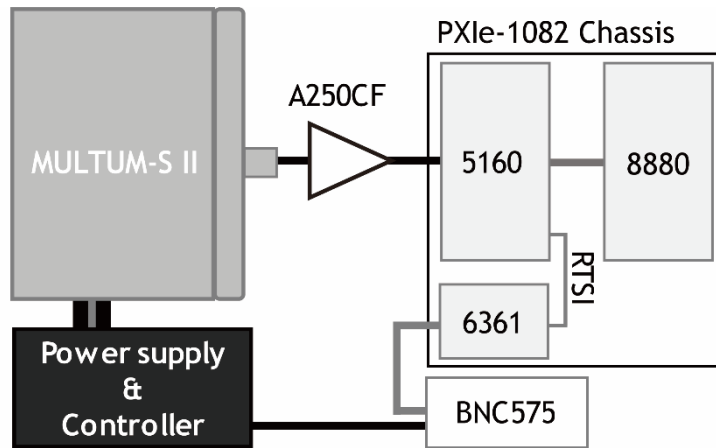
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278

279 Figure 1. (a) Schematic of electrostatic-induced charge detector (iCD) installed in
 280 MULTUM-S II and ion detection using a secondary EM detector (b) Schematic of charge
 281 readout for ion packet charged $+Q$.

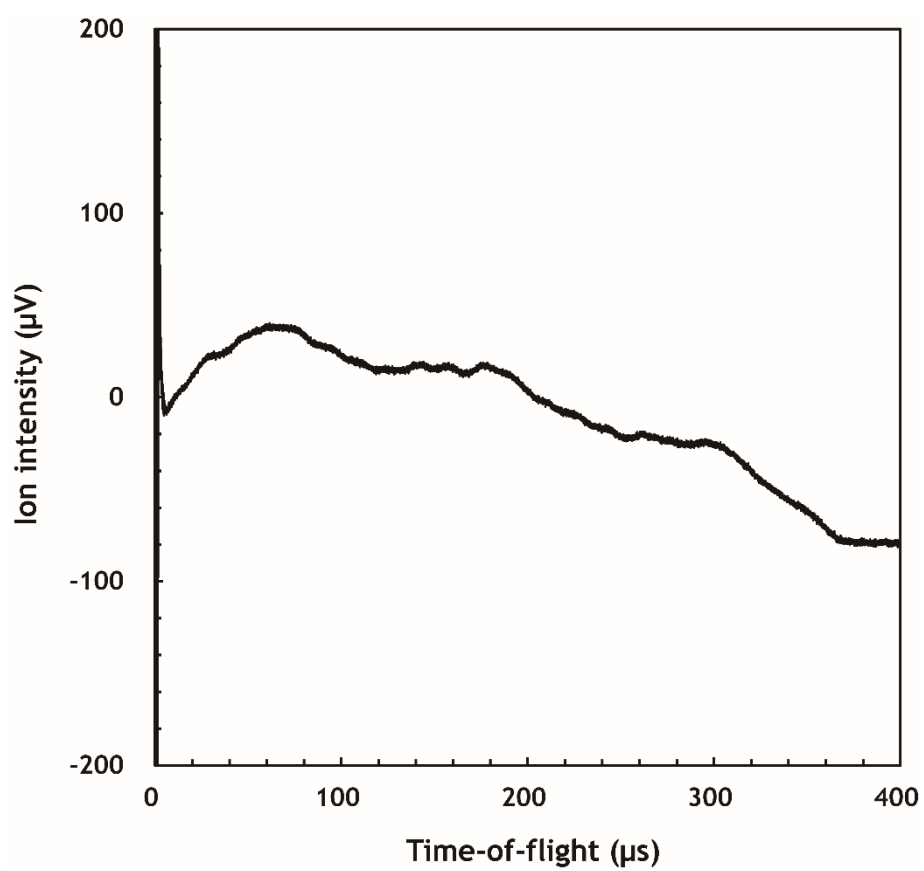
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284 Figure 2. Schematic of data acquisition system for iCD. Outputs from A250CF
 285 preamplifier are converted to 10-bits digital signals using PXIe-5160 (5160) digitizer. The
 286 digital signals are processed and stored by PXIe-8880 (8880). BNC575 and PXIe-
 287 6361(6361) controls timing for data acquisition.

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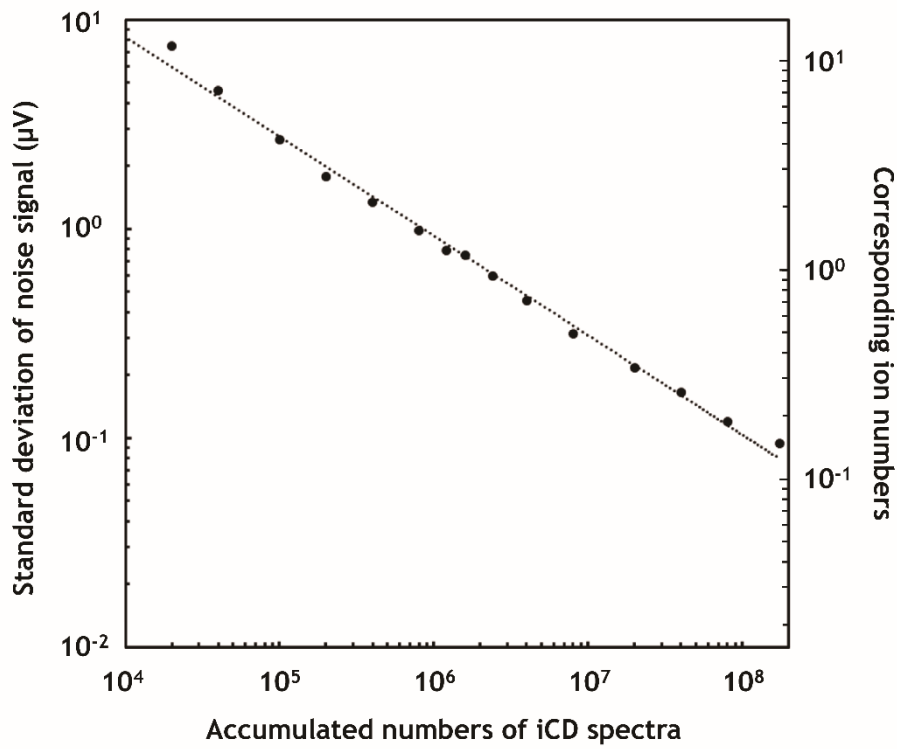


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290 Figure 3. Baseline of an iCD spectrum, of which accumulation of the iCD spectra was

291 2.4×10^6 .

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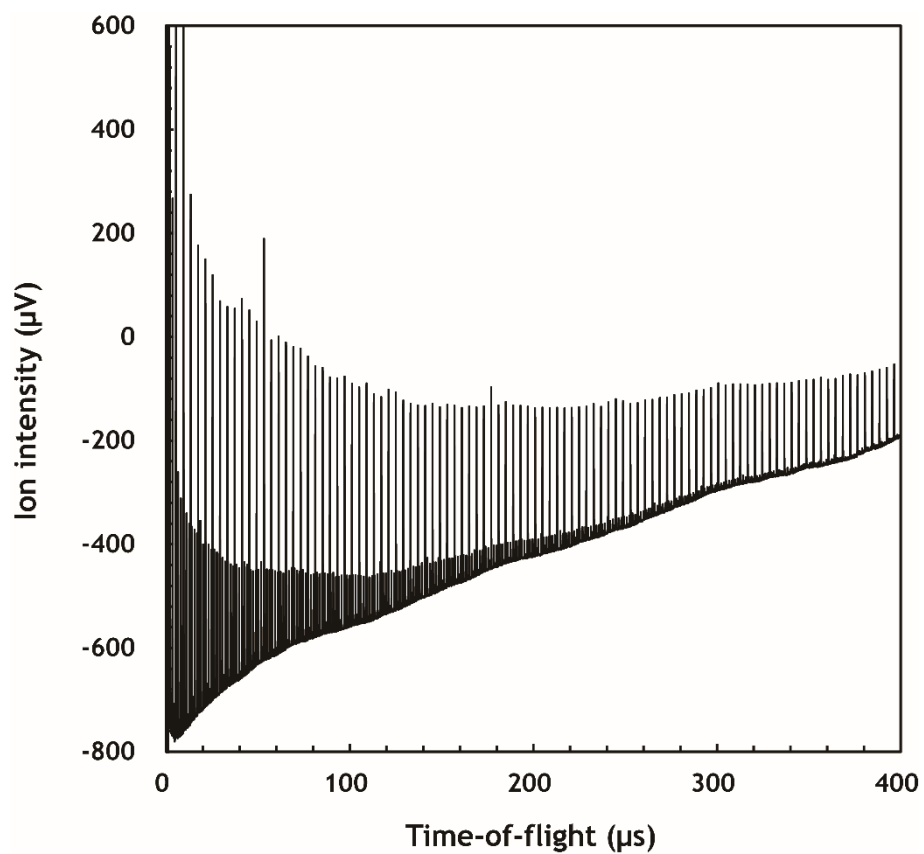


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294 Figure 4. Standard deviations of noise signal as a function of accumulated numbers of
 295 iCD spectra. Dotted line represents a power approximate expression (y (μV) = $664.0 x^{-0.476}$).

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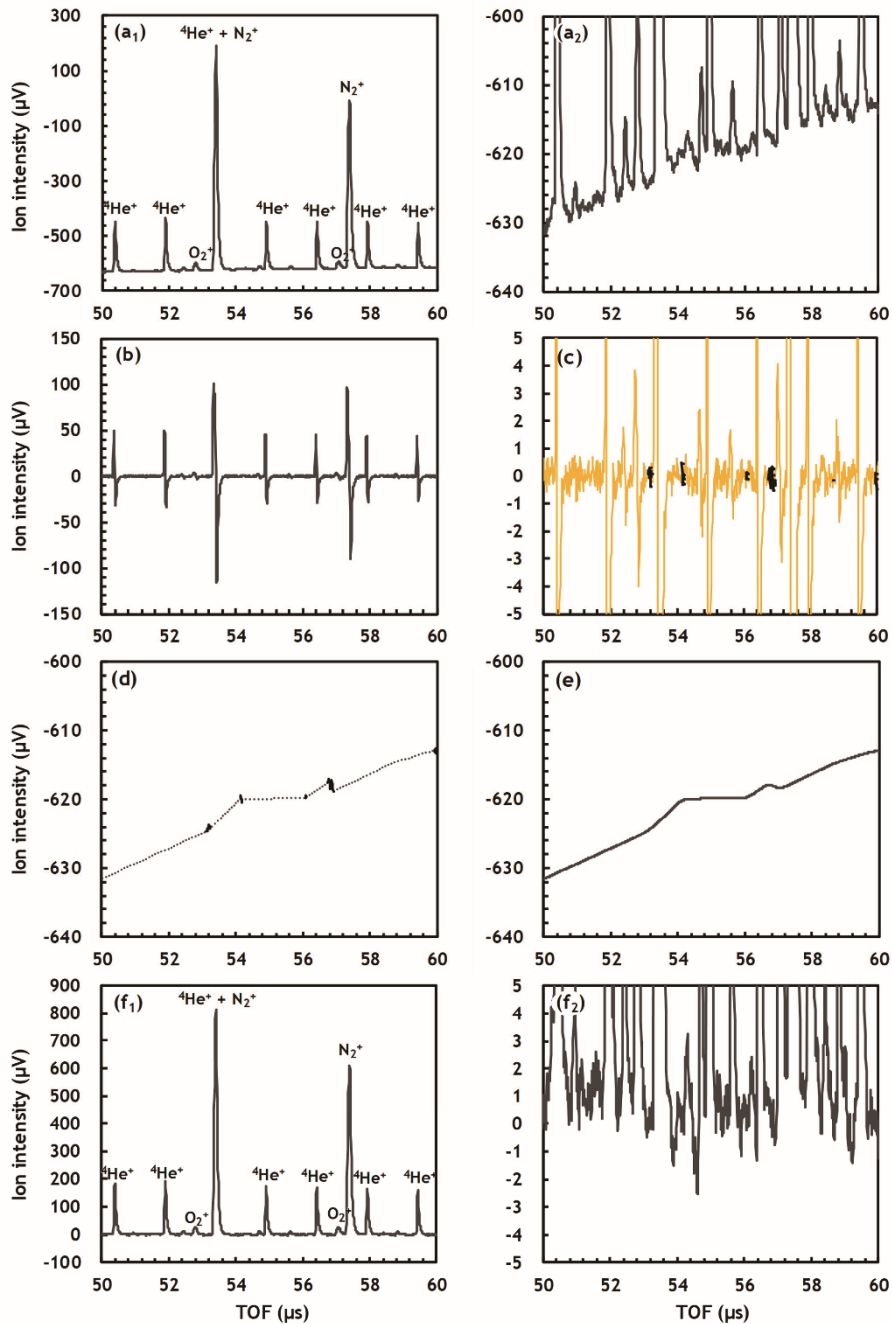
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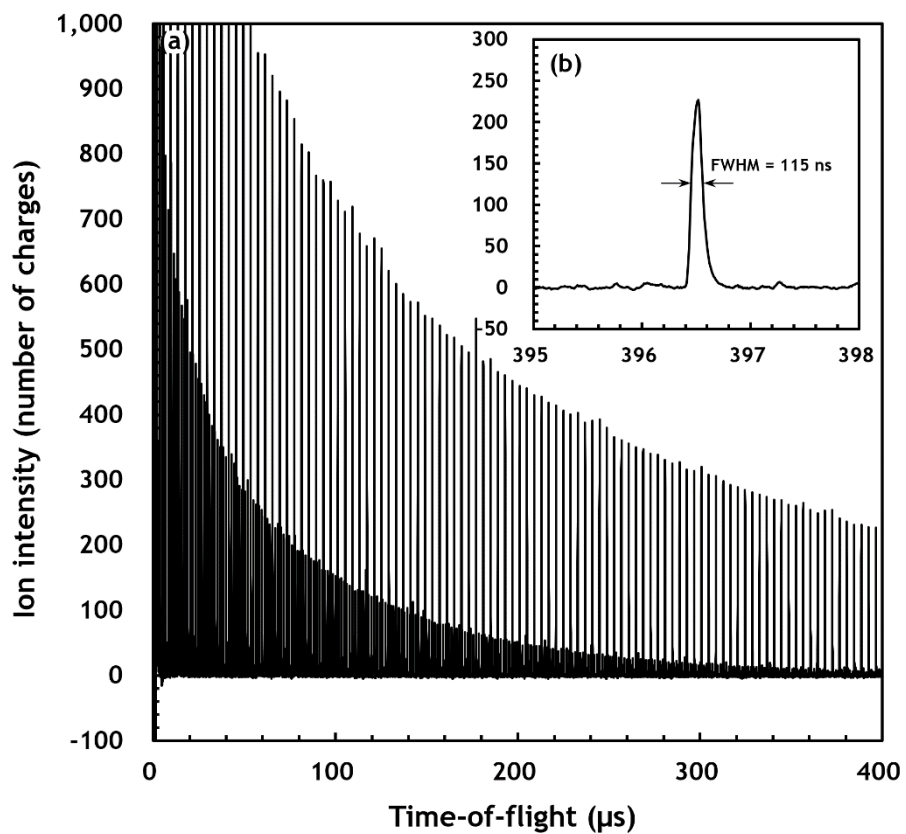
299 Figure 5. iCD spectrum of N₂-He gas.

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Figure 6. Procedure of baseline correction. (a₁) An enlarged iCD spectrum of Figure 5 (50 μs to 60 μs). (a₂) An enlarged iCD spectrum of the baseline of (a₁). (b) A differential iCD spectrum of (a₁). (c) An enlarged differential iCD spectrum of (b). Ion and noise signals are shown in yellow and black, respectively. (d) The noise signals of (c) are removed and interpolated linearly (dotted line). (e) Smooth profile of (d) as modulated baseline profile of (a₂). (f₁) A baseline-corrected iCD spectrum. Full spectrum is shown in Figure 7. (f₂) An enlarged baseline-corrected iCD spectrum of (f₁).

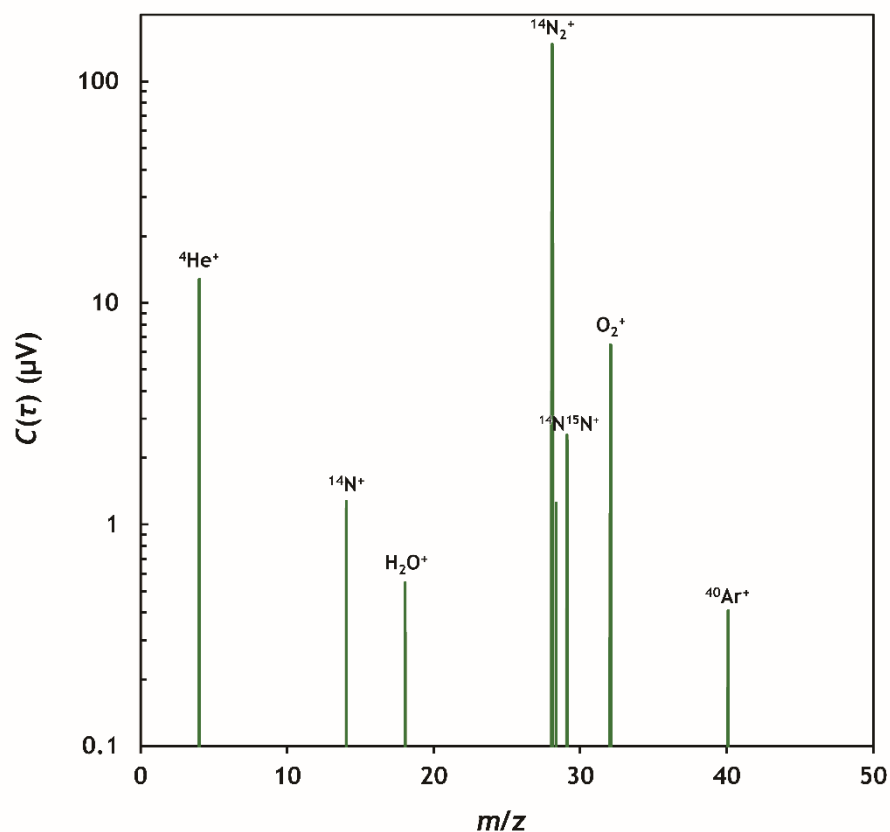


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310 Figure 7. (a) Baseline-corrected iCD spectrum of $\text{N}_2\text{-He}$ gas. (b) A spectrum at 396.5

311 μs .

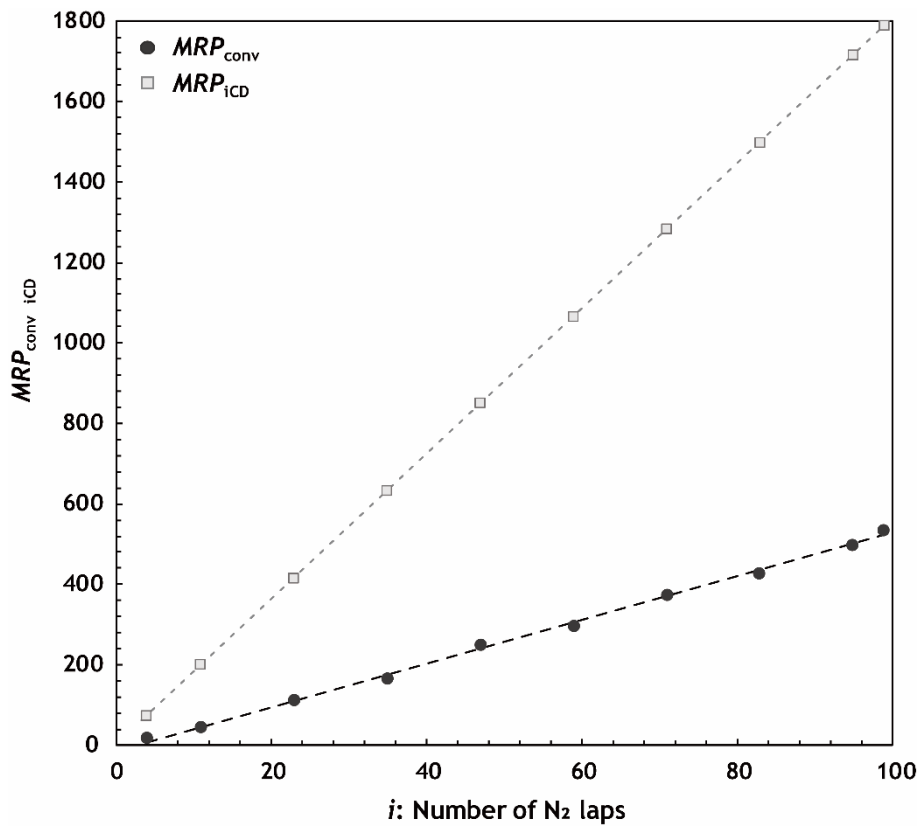
312



313

314 Figure 8. Convolved mass spectrum of $\text{N}_2\text{-He}$ gas calculated from iCD spectrum. τ_{\min} ,
 315 τ_{\max} , s_τ , t_0 , Δt and V_{dis} were set at 0.96 μs , 4.80 μs , 0.5 ns, 0.3781 τ , 288 ns, and 0.6 μV ,
 316 respectively. The m/z (horizontal axis) is calculated from τ using internal mass
 317 references at m/z 4.00260 ($^4\text{He}^+$) and 28.00615 ($^{28}\text{N}_2^+$).

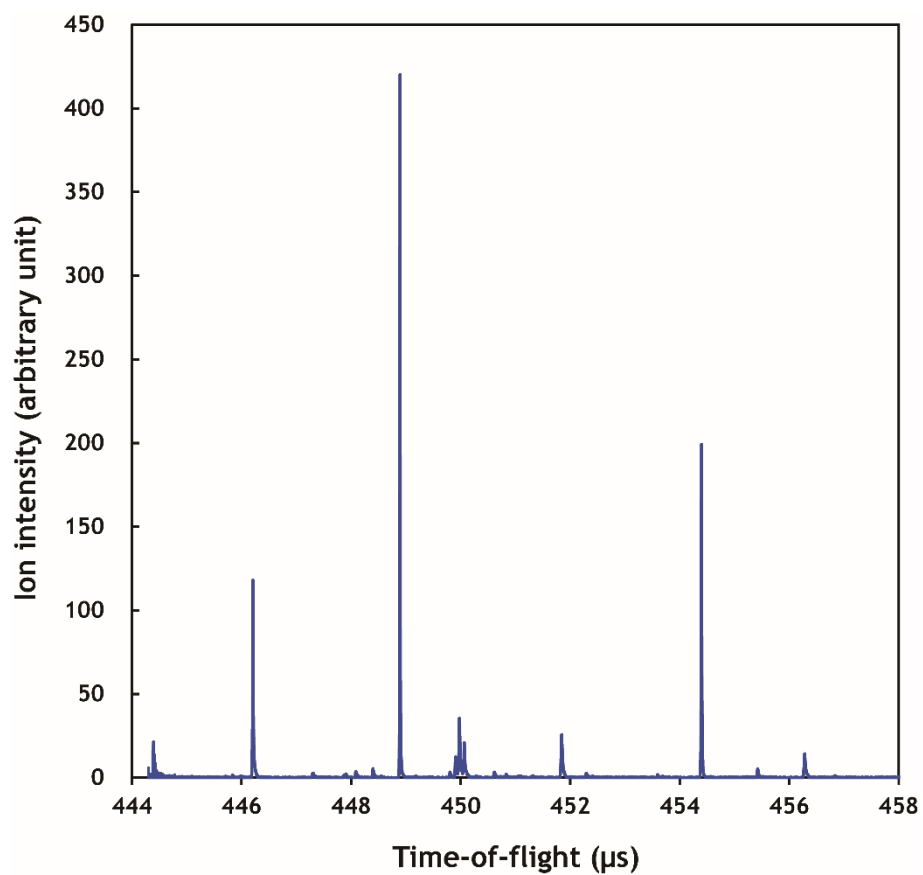
318



319

320 Figure 9. Change of MRP_{conv} and MRP_{iCD} of N_2^+ as a function of number of multiturn
 321 laps.

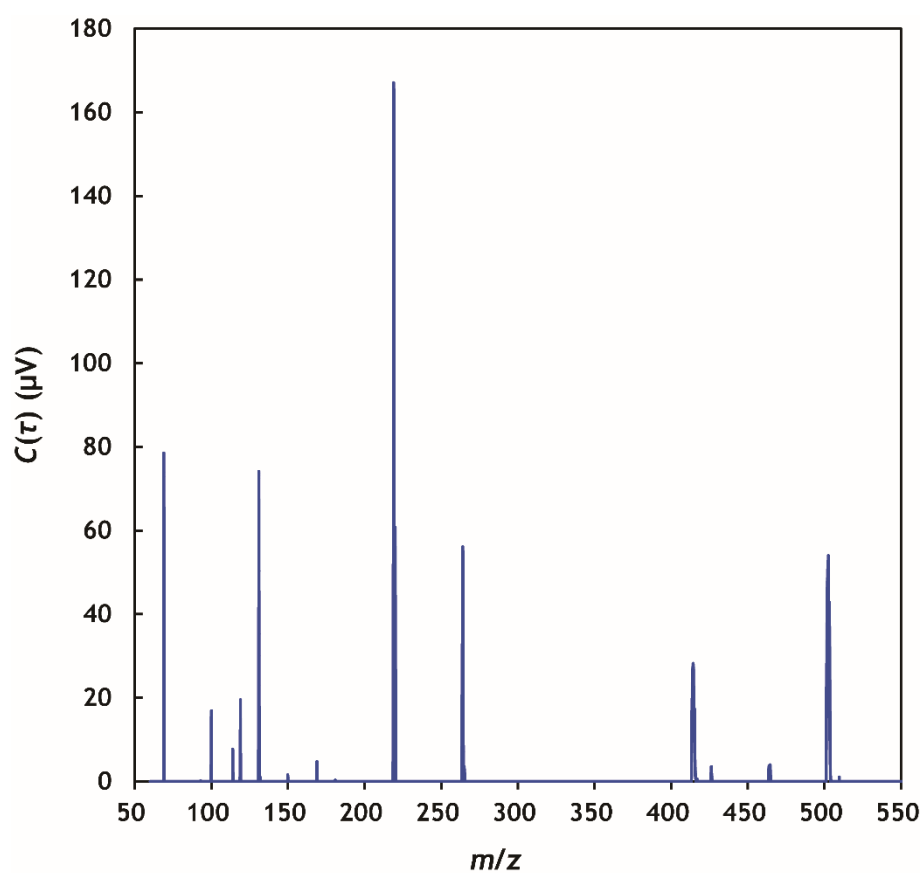
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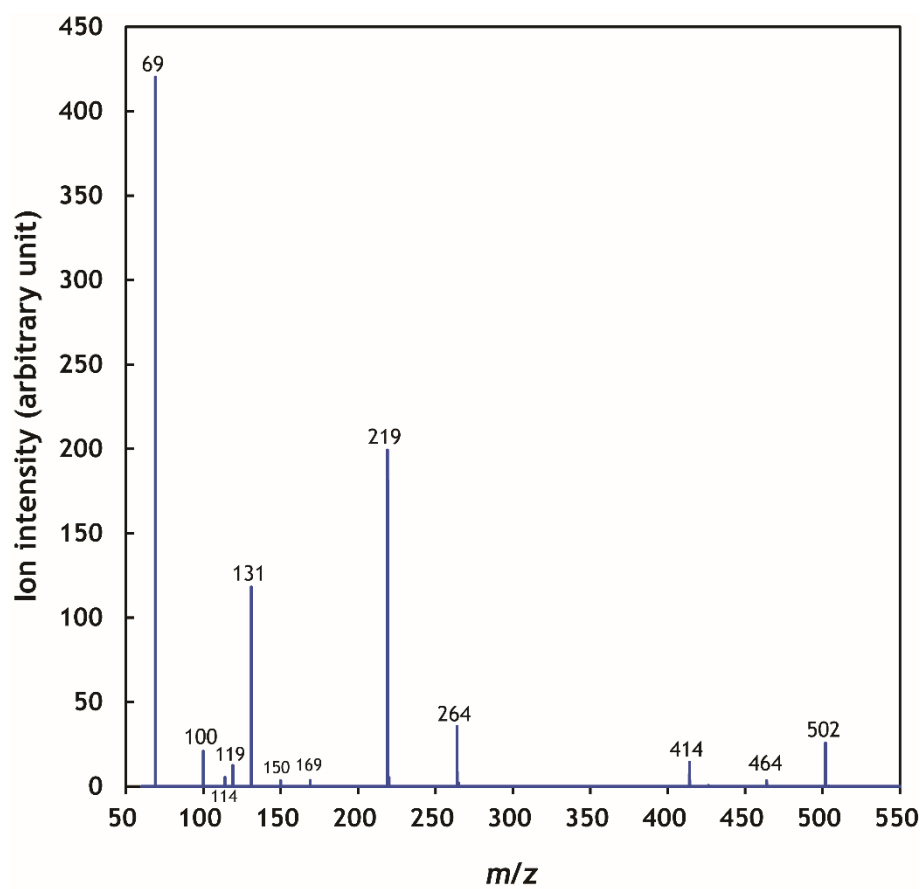
323

324 Figure 10. Multiturn TOF spectrum of PFTBA extracted from the multiturn trajectory.

325



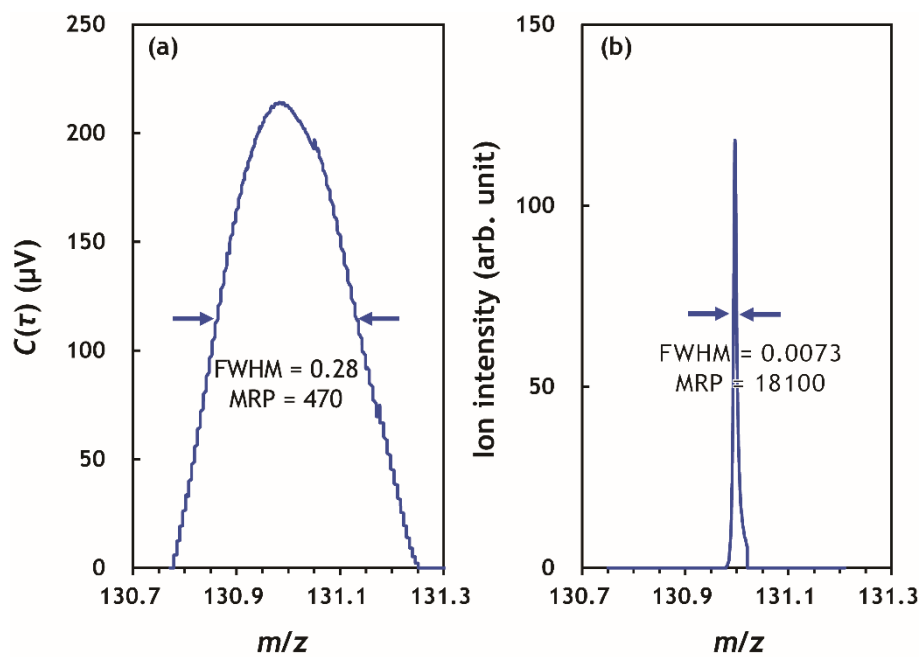
326
 327 Figure 11. Convolved mass spectrum of PFTBA calculated from iCD spectrum. τ_{\min} ,
 328 τ_{\max} , s_{τ} , t_0 , Δt and V_{dis} were set at 5.76 μs , 17.28 μs , 0.0638 ns, 0.3781 τ , 384 ns, and 0 V
 329 respectively. The m/z (horizontal axis) is calculated from τ using internal mass
 330 references of m/z 68.9952 (CF_3^+) and 218.9856 (C_4F_9^+).
 331



332

333 Figure 12. Extended convolved mass spectrum of PFTBA.

334



335

336 Figure 13. Peak shapes at m/z 130.9920 ($C_3F_5^+$) (a) from Figure 11, (b) from Figure 12.

337

338 Table 1. molecular formulas, exact masses, measured masses, mass differences (Δm),
 339 mass accuracies, number of laps, and mass resolution (MRP) of major peaks from PFTBA
 340 sample.

Molecular formula	Exact mass	Measured mass	$\frac{\Delta m}{\times 10^{-3}}$	Mass accuracy ppm	Number of laps	MRP
CF ₃	68.9952	68.9952	0.0	0	71	28200
C ₂ F ₄	99.9936	99.9897	3.9	39	59	10800
C ₃ F ₄ H ₂	113.9973	113.9926	4.7	42	55	9000
C ₂ F ₅	118.9920	118.9876	4.4	37	54	10800
C ₃ F ₅	130.9920	130.9897	2.4	18	51	18100
C ₃ F ₇	168.9888	168.9797	9.1	54	45	7300
C ₄ F ₉	218.9856	218.9856	0.0	0	40	20500
C ₄ F ₉ H	219.9935	219.9752	18.3	83	40	10300
C ₅ NF ₁₀	263.9877	263.9807	7.1	27	36	9600
C ₅ NF ₁₀ H	264.9956	265.0001	-4.5	17	36	9800
C ₈ NF ₁₆	413.9782	413.9701	8.1	20	29	8700
C ₉ NF ₁₈	463.9750	463.9589	16.1	35	27	6900
C ₉ NF ₂₀	501.9718	501.9678	4.0	8	26	8500

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