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Simultaneous positive and negative HRAM acquisition using a Q-TOF mass spectrometer with ultra-high mass stability

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Overview

◆ To enable simultaneous positive and negative ion mode MS acquisition on a Q-TOF system, we developed a novel conversion equation for calculating *m/z* from the measured TOF that compensates for the high-voltage instability after polarity switching.

◆ By applying this algorithm to Shimadzu LCMS-9050 (**Fig. 1**), it was demonstrated that 600 msec polarity switching time was sufficient for simultaneously achieving low-ppm mass accuracies in both positive and negative modes.

Fig. 1

Prototype version of Shimadzu LCMS-9050 was used for this investigation.

1. Introduction

◆ Quadrupole time-of-flight mass spectrometers (Q-TOF) are a powerful and robust tool for high-resolution accurate-mass (HRAM) data acquisition. However, even though Q-TOF are capable of running in both positive and negative ion modes, it is widely considered impractical to run the two modes in a single LC-MS analysis.

◆ Polarity switching typically results in a considerable compromise in the accuracy of measured masses, observed as a mass shift that continues for hours after polarity switching. The cause of this phenomenon is the instability of high voltages (several kV) applied to TOF components, which occurs as a result of shifting the voltage across a large amplitude during the switching event. We introduce a new system that mitigates the above issue.

2. Concept

◆ In a time-of-flight mass spectrometer, the relationship between the time-of-flight "t" and the mass to charge ratio "m/z" is commonly employed [Equation A].

$$E = qV = \frac{1}{2}mv^2$$

$$t = a\sqrt{m/z} + b \qquad [A]$$

Note:
V : potential of the ion
q : charge of the ion
m : mass of the ion
v : velocity of the ion
a, b : constant parameters

◆ This equation assumes that the high voltage applied to the TOF system is constant. However, this is far from reality when polarity switching takes place. The polarity switching time (**Fig. 2**) depends on stray capacity of metal parts such as flight tube or ion reflector and characteristics of power source, and it typically takes several seconds to fully stabilize the power source voltage.

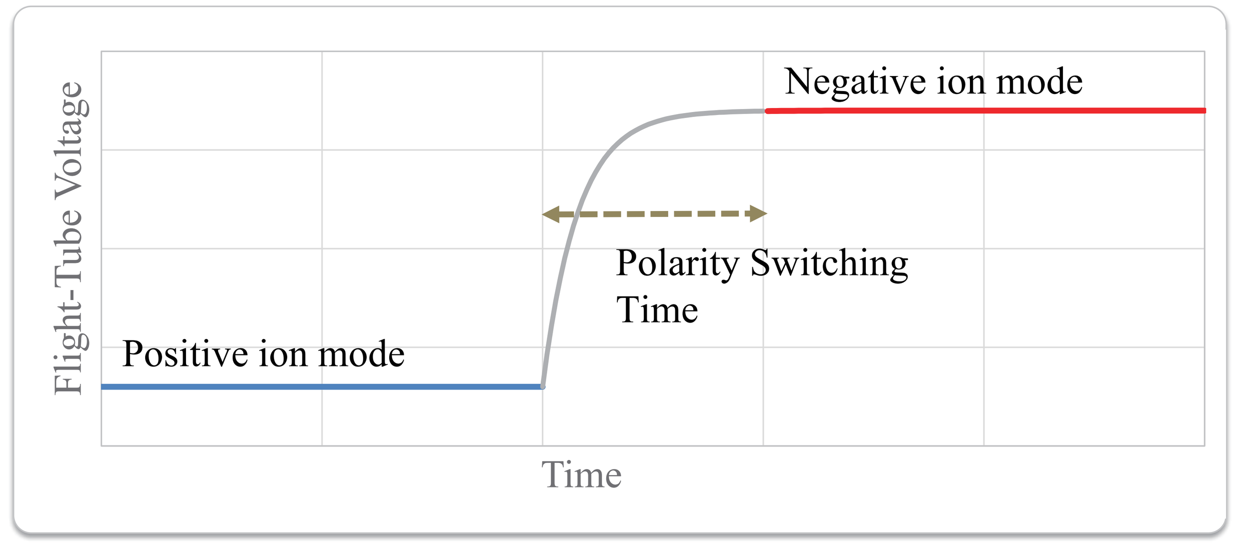

Fig. 2 The transient barrier to fast polarity switching. Seconds of polarity switching times are required to achieve high mass accuracy after polarity swithing.

◆ To shorten the effective polarity switching time, we introduced a new term representing the *time elapsed after the polarity switching was initiated* to [Equation A].

◆ The correction term was expressed as function $f(t_p, t_a)$ where "t_p" is the elapsed time after the polarity switching and "t_a" is the data acquisition time (**Fig. 3**).

◆ Equations for "t" and "m/z" including the correction terms "$f(t_p, t_a)$" are given in [Equation B].

$$t = \left(a - f(t_p, t_a)\right) \cdot \sqrt{m/z} + b \qquad [B]$$

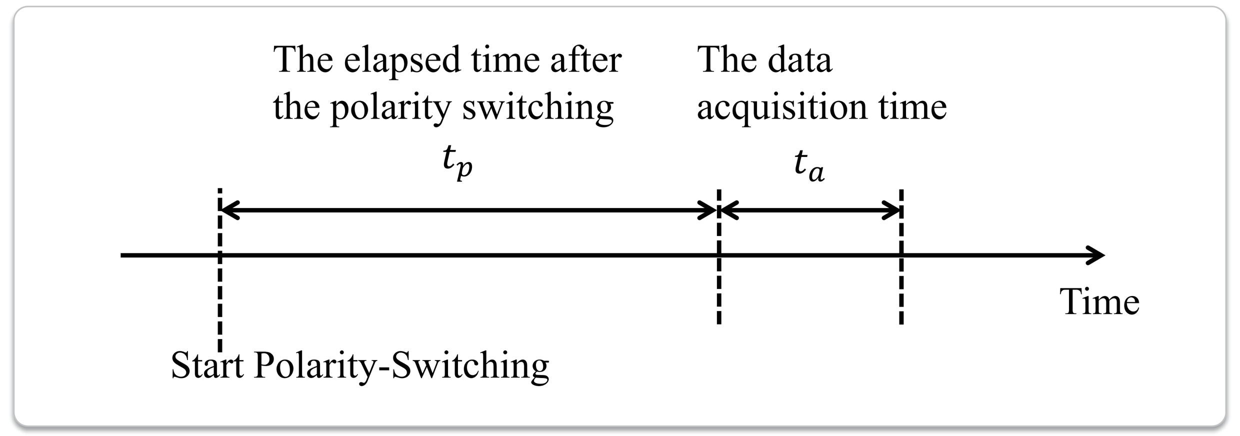

Fig. 3 A schematic diagram showing the concepts of t_p, t_a.

3. Result

◆ When the mass error after the switching of positive and negative ions was obtained using [Equation A], the mass accuracy was stabilized about 1 second after the polarity switching, but the mass shift occurred in the subsecond region.

◆ Using the result obtained by [Equation A], the parameter of the correction term was decided, and subsequently an additional data acquisition was carried out by [Equation B].

◆ The correction term resulted in a dramatic improvement in mass accuracy. (**Fig.4**)

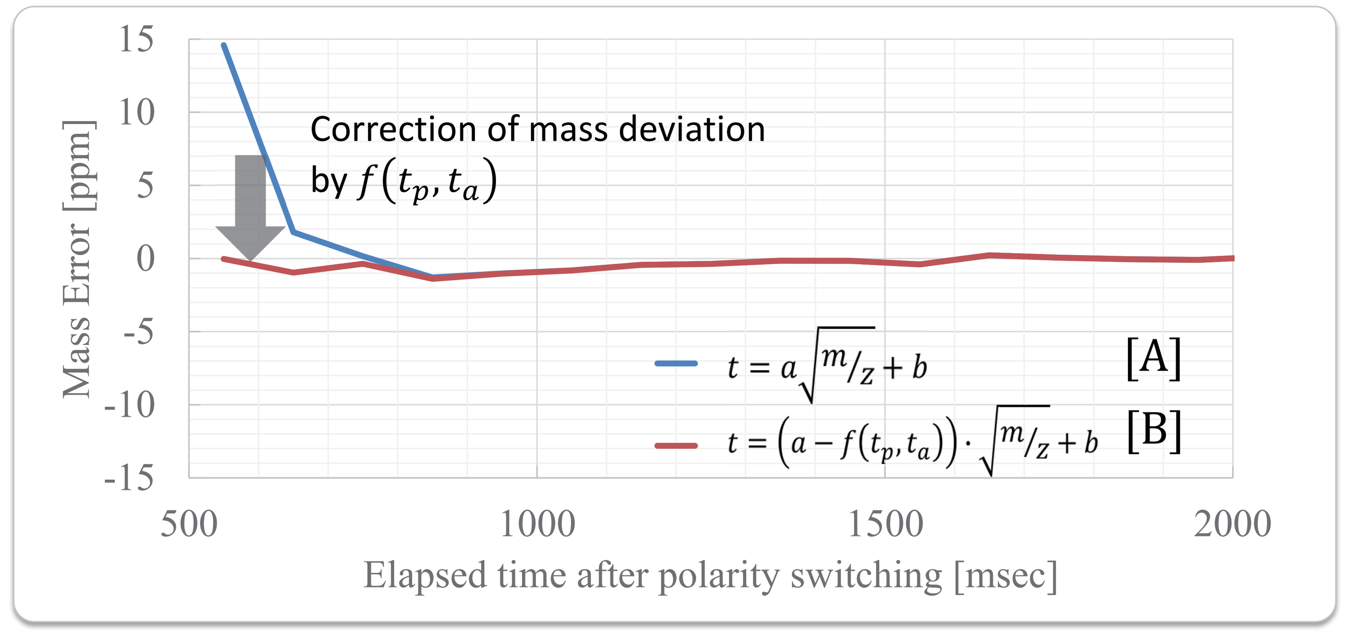

Fig. 4 Results of mass accuracy measurement.
The measured mass is sodium iodide $[NaI]_6Na^+$ (theorical m/z is 922.3547), the standard sample of Shimadzu Q-TOF.

◆ The mass error in the simultaneous positive and negative measurements was examined in a wide range of m/z by introducing the correction term, the mass accuracy improvement effect was observed. (**Table 1**)

Table 1 Mass error measurement results of sodium iodide during simultaneous positive and negative ion measurements at t_p=600 ms and t_a=50 ms

Positive-ion	$[NaI]Na^+$	$[NaI]_3Na^+$	$[NaI]_6Na^+$	$[NaI]_{10}Na^+$	$[NaI]_{13}Na^+$
m/z	172.8834	472.6727	922.3562	1521.9337	1971.6166
Mass Error [ppm]	-0.87	-0.53	-0.60	-0.54	-0.67
Negative-ion	$[NaI]I^-$	$[NaI]_2I^-$	$[NaI]_4I^-$	$[NaI]_6I^-$	$[NaI]_{10}I^-$
m/z	276.8004	426.6950	726.4849	1026.2748	1625.8538
Mass Error [ppm]	2.02	2.15	2.4	2.03	2.67

◆ Long-term mass stability was confirmed using the antibiotic reference standard (with molecular weights from 150 to 1100 Da) , accurate mass values within 3 ppm were obtained under room temperature environment. (**Fig.5**)

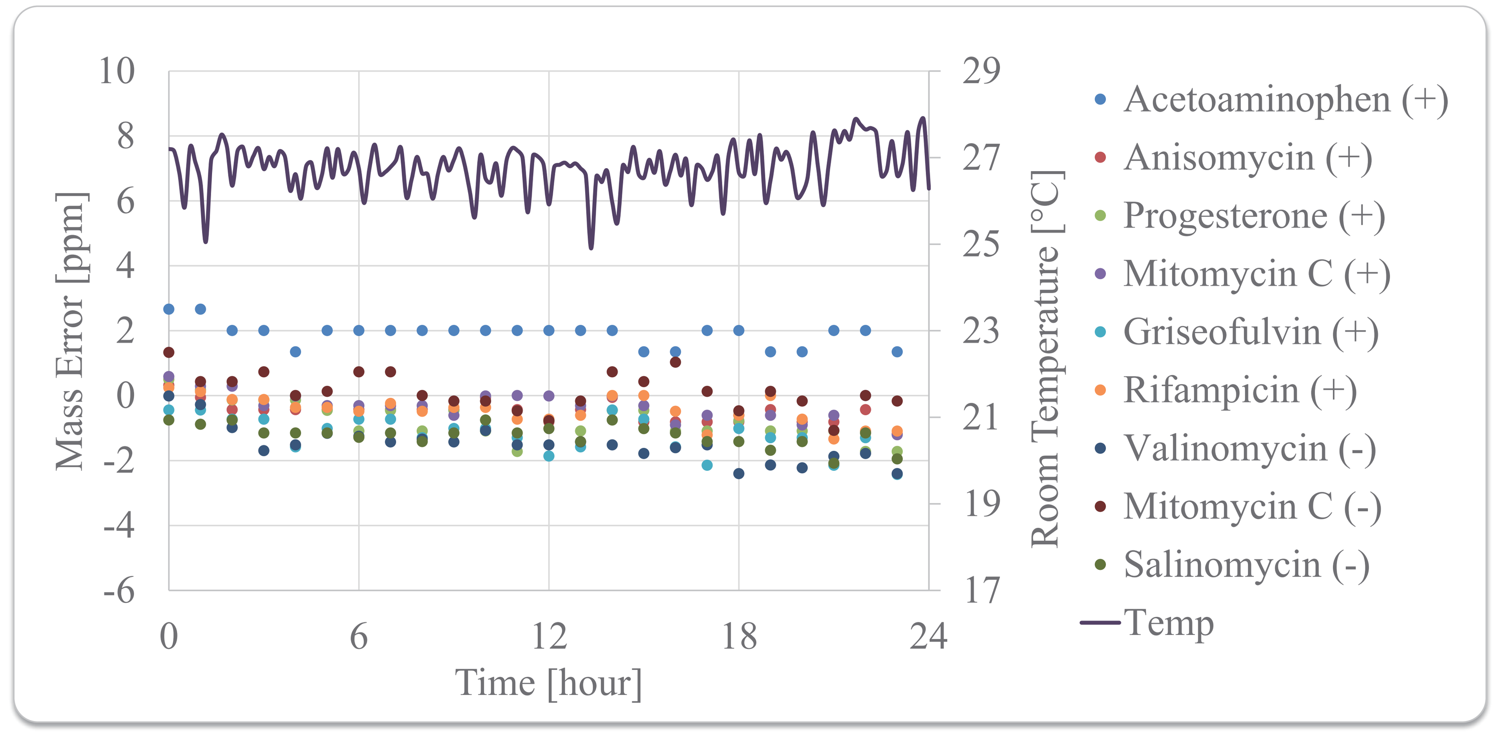

Fig. 5 Results of long-term mass accuracy measurement.

4. Conclusion

✓ The calibration algorithm compensates for the high-voltage instability and achieves low-ppm mass accuracy with polarity switching.

✓ The LCMS-9050 increases analytical throughput because it can measure both positive and negative ions at the same time based on analytical objectives.

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