

# Development and Application of Miniaturized High-resolution Time-of-Flight Mass Spectrometer "MULTUM-S II"

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## Overview

**[Purpose]** To develop a miniature mass spectrometer with high mass resolution and evaluate the performance.

**[Experimental Methods]** Mass accuracy was evaluated using PFTBA. To demonstrate doublet separation, mixture gas of greenhouse gases (N<sub>2</sub>O and CO<sub>2</sub>) was used. In the PCB analysis, C-180S-TP (2', 2', 3, 4, 4' 5, 5'-Heptachlorobiphenyl) was used.

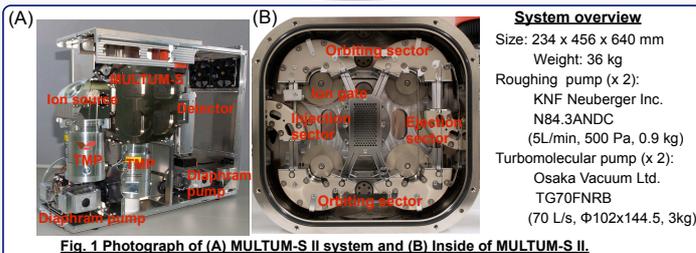
**[Results]** Mass accuracy was less than 5 ppm. Mass resolution was > 40,000 and doublets of CO<sub>2</sub>&N<sub>2</sub>O ( $\Delta m = 0.0113$ ) were clearly separated.

**[References]**  
 1. Shimma S, Nagao H, Aoki J, Takahashi K, Miki S, Toyoda M. *Anal. Chem.*, 82, 8456 (2010)  
 2. Ichihara T, Uchida S, Ishihara M, Katakuse I, Toyoda M. *J. Mass Spectrom. Soc. Jpn.*, 55, 363 (2007)

## Introduction

In our laboratory, a home built miniature multi-turn time-of-flight (TOF) analyzer was constructed and named "MULTUM-S"<sup>1</sup>. Subsequently "MULTUM-S II (infiTOF)"<sup>2</sup>, which has improved manufacturing precision and newly designed electrodes, has been constructed. These instrument basically consists of four electric sectors and two additional electric sectors for purpose of ion injection/ejection. The size and weight of the system is 234 mm x 456 mm x 640 mm and 36 kg (including vacuum pump and electronic circuits).

## Instrument



**System overview**  
 Size: 234 x 456 x 640 mm  
 Weight: 36 kg  
 Roughing pump (x 2): KNF Neuberger Inc. N84.3ANDC (5L/min, 500 Pa, 0.9 kg)  
 Turbomolecular pump (x 2): Osaka Vacuum Ltd. TG70FNRB (70 L/s,  $\Phi 102 \times 144.5$ , 3kg)

Fig. 1 Photograph of (A) MULTUM-S II system and (B) Inside of MULTUM-S II.

## Geometry and ion optics of MULTUM part

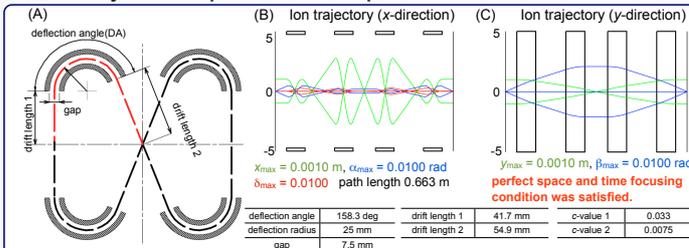


Fig. 2 (A) Ion trajectories in a multi-turn TOF mass spectrometer with the half size of MULTUM II using TRIQ-DRAW. (A) Geometry of multi-turn part. (B) x-direction view, and (C) y-direction view.

## Geometry and ion optics of injection/ejection part

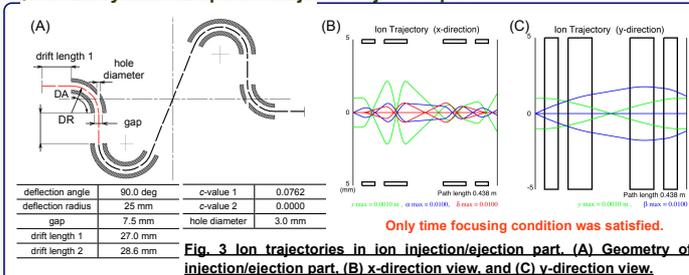


Fig. 3 Ion trajectories in ion injection/ejection part. (A) Geometry of injection/ejection part. (B) x-direction view, and (C) y-direction view.

## Operation of MULTUM-S II

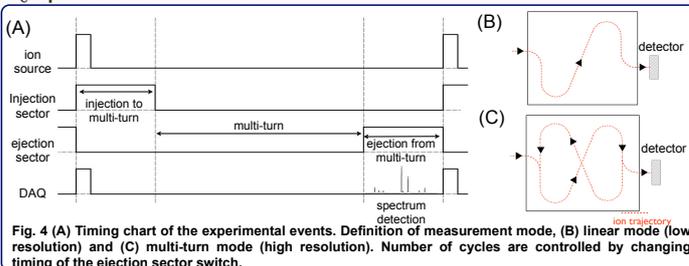


Fig. 4 (A) Timing chart of the experimental events. Definition of measurement mode. (B) linear mode (low resolution) and (C) multi-turn mode (high resolution). Number of cycles are controlled by changing timing of the ejection sector switch.

## Results

### Mass accuracy

Sample: PFTBA		Measured TOF:		Examination: calibrate C <sub>3</sub> F <sub>5</sub> peak (m/z 130.9920) using CF <sub>3</sub> or C <sub>4</sub> F <sub>9</sub> , or both (in 2 point calibration). Methods: measure TOF of each peak (2GS/s) at 30 and 60 cycles. After that, calculate TOF per cycle (see left table).
Formula	M <sup>exact</sup> mass	Formula	TOF/cycle (us)	
CF <sub>3</sub>	68.9952	CF <sub>3</sub>	6.88655(1)	
C <sub>3</sub> F <sub>5</sub>	130.9920	C <sub>3</sub> F <sub>5</sub>	9.48877(2)	
C <sub>4</sub> F <sub>9</sub>	218.9856	C <sub>4</sub> F <sub>9</sub>	12.26848(3)	

**Result of 1 point calibration:**  
 130.9996 (by m/z 69) → 7.6 mDa shift  
 130.9875 (by m/z 219) → 4.5 mDa shift

**Result of 2 point calibration:**  
 130.9926 ± 0.6 mDa (4.2 ppm)  
 → 0.6 mDa shift from theoretical value

To ensure high accuracy and precision, multi point calibration is essential.

### CO<sub>2</sub> and N<sub>2</sub>O separation and accurate mass measurement

Real-time monitoring of nitrous oxide (N<sub>2</sub>O) is required to elucidate the generating mechanism and investigate its trend of spread. N<sub>2</sub>O is known as a greenhouse gas, and the warming effect is about 310 times larger than carbon dioxide (CO<sub>2</sub>). Furthermore, N<sub>2</sub>O is one of the ozone-depleting substances. If we try to carry out real-time monitoring of N<sub>2</sub>O using mass spectrometry, a mass spectrometer with high mass resolution is required, because the nominal mass of N<sub>2</sub>O is the same as that of CO<sub>2</sub>. If we would like to separate CO<sub>2</sub> and N<sub>2</sub>O doublet completely, the required mass resolution is about 10,000. Conventional portable field instruments are incapable of this measurement because of low mass resolution. Here, we demonstrate the feasibility of using the InfiTOF for high-resolution N<sub>2</sub>O analysis using N<sub>2</sub>O standard gas.

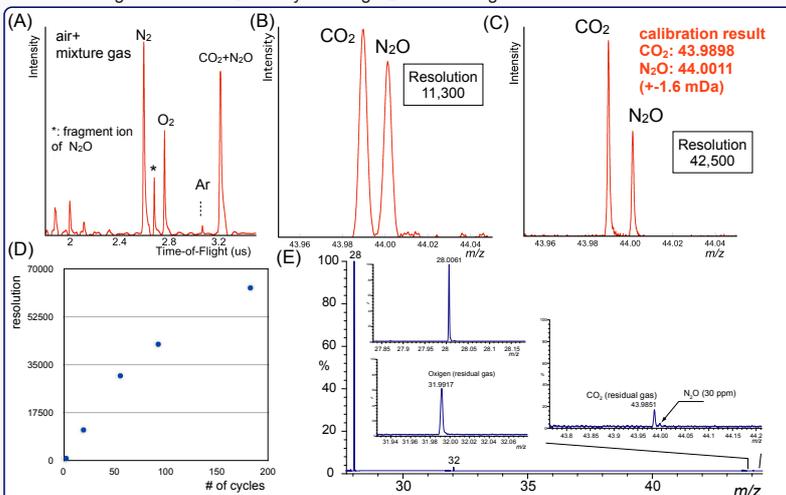


Fig. 5 Separation of CO<sub>2</sub>&N<sub>2</sub>O doublet. (A) control spectrum (air+mixture gas); (B,C) doublet spectra after 20 cycles and 100 cycles; (D) Variation of mass resolution; (E) Simultaneous measurement of N<sub>2</sub> and N<sub>2</sub>O (30 ppm).

### PCB measurement with high mass resolution and high sensitivity

High-resolution selected ion monitoring (HRSIM) provides sensitive and selective detection for compounds of environmental interest such as polychlorinated biphenyls (PCB's). The analysis as traditionally carried out by using magnetic sector mass spectrometers is highly effective. However, setup and method development can be complicated, requiring careful programming of SIM target masses, lock masses, and retention time groups. Magnetic sector mass spectrometers with a resolving power of 10,000 or greater tend to be large and expensive.

Time-of-flight mass spectrometry (TOFMS) is an attractive alternative because there is little or no tradeoff between high resolution and high sensitivity. However, previous commercially available GC/TOFMS systems are not offered with a resolving power of 10,000 or greater. The InfiTOF is well suited for PCB analysis. The system is compact, portable, and capable of achieving a resolving power of >40,000. By acquiring high-resolution mass spectra in segments, method development is made easier.

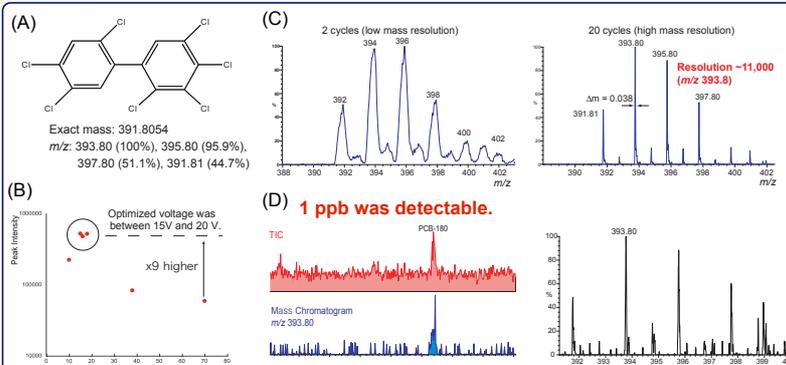


Fig. 6 (A) Structure of C-180S-TP; (B) Optimization of ionization voltage (70 V is typical value); (C) Comparison of mass spectra of PCB-180S-TP (2 cycles and 20 cycles); (D) TIC, mass chromatogram and obtained mass spectrum of m/z 393.8 in 1 ppb.

## Conclusion

- The high mass resolution of > 30,000 is available even in the miniaturized instrument.
- To ensure high mass accuracy and precision, multi point calibration is essential.
- Doublets of CO<sub>2</sub> and N<sub>2</sub>O were clearly separated.
- The LOD of PCB was 1 ppb.