SHIMADZU

Development of oxygen attachment dissociation (OAD)-TOF system incorporating a modified collision cell

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1. Introduction

- Oxygen Attachment Dissociation (OAD)[1-3] is a novel radical-induced dissociation technology that utilizes charge-neutral hydroxyl radicals (OH•) and oxygen atoms (O•). The introduction of OH•/ O• into a collision cell initiates radical-induced dissociation, which is distinct from CID. OAD provides double-bond-specific fragmentations within carbon chains (C=C).
- Although time-of-flight MS (TOF) is ideal for accurately annotating OAD product ions, TOF systems require high vacuum levels, making it difficult to introduce radicals into the collision cell at high flow rates. In this study, a new radical source and collision cell were developed to facilitate the OAD reaction, even at a low flow rate of radicals.

1) Takahashi.H et al. Anal. Chem. 2018, 90 (12), 7230-7238.
2) Takahashi.H et al. Mass Spectrometry. 2019, S0080.
3) Uchino.H et al. Commun. Chem. 5, 162 (2022).

OAD MS/MS

Neutral radical-based

Charge-neutral radical-induced dissociation is available in both positive and negative ion modes!

O• OAD (Oxygen Attachment Dissociation)-MS/MS

$[M+H]^+ + O^\bullet \rightarrow [M+H+O]^{+\bullet} \rightarrow$ *fragments*

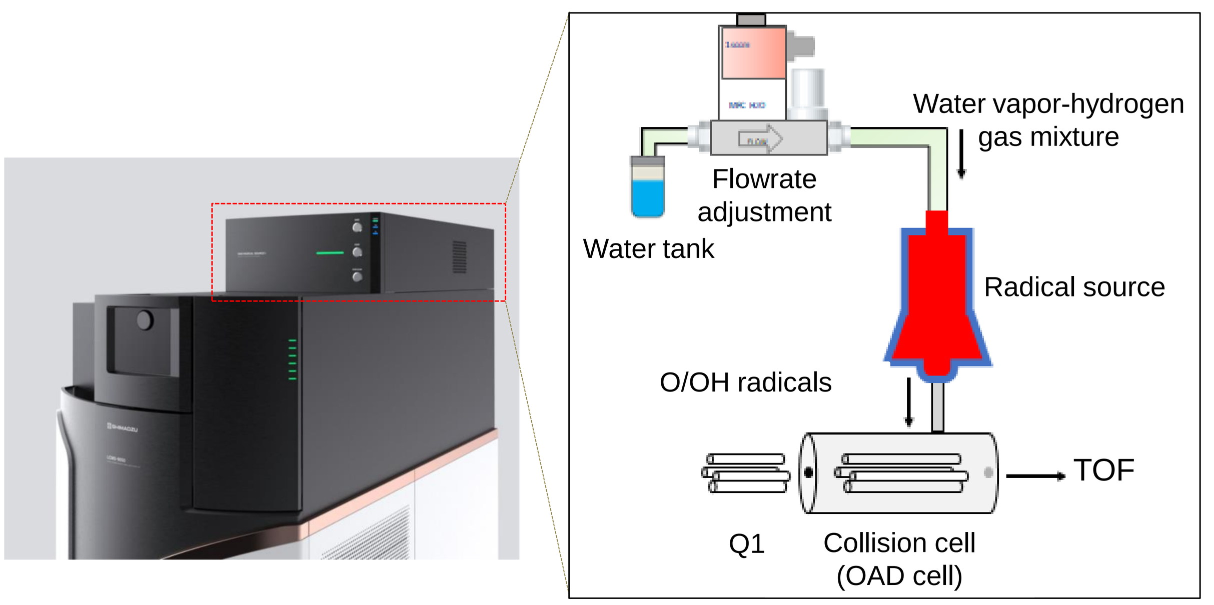

Fig. 1. Shimadzu OAD-TOF system.

2. Radical source

- The magnetic field passes through the quartz tube of the radical source, with microwaves (2.45 GHz, ~30 W) supplied to a spiral antenna wrapped around the quartz tube. Water vapor and hydrogen gas are converted into radicals via microwave discharge.
- OH•/ O• possess strong oxidizing power and can cause the electrode to oxidize, thereby disrupting the electric field within the collision cell. To counteract this, the radical source generates H• from hydrogen to reduce the electrode.
- The diameter of the quartz tube outlet is narrowed, which not only increases the pressure within the tube to facilitate plasma generation, but also prevents ions from being transported to the collision cell.

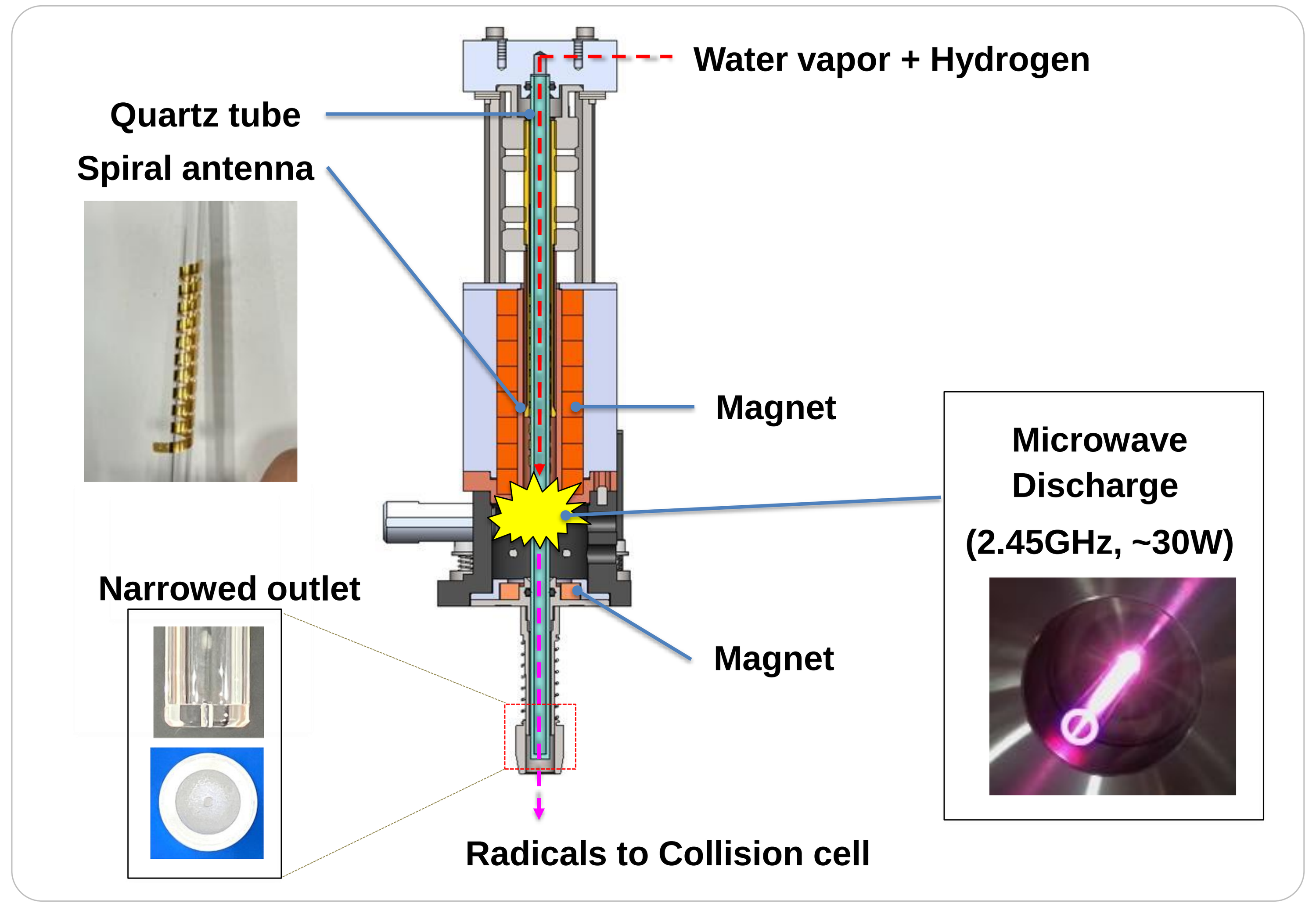

Fig. 2. Schematic diagram of the radical source

3. Collision cell

- The metal surface exhibits a high recombination coefficient γ for radicals (for example, γ of Fe is 0.010±0.004)[4]. Consequently, radicals readily recombine into stable molecular forms on the metal surface inside the collision cell.
- Conversely, it is known that the recombination coefficient γ of insulators is lower than that of metals. (for example, γ of Pyrex is $(1.3\pm0.3)\times10^{-4}$)[4].

4) DOI:10.1039/TF9716700198

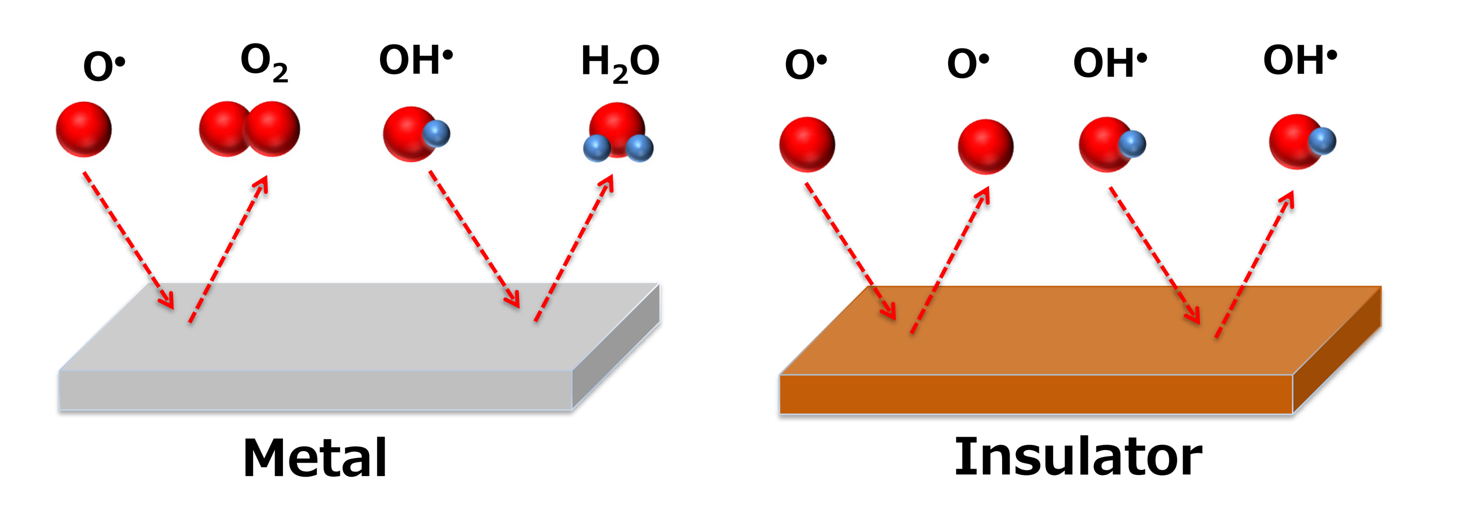

Fig. 3. A model of radical recombination on metal/insulator surfaces.

- To reduce the exposure of the metal surface, a polyimide film was attached to the inner wall of the collision cell. This significantly improved the radical density in the cylinder of the collision cell.
- We designed the collision cell's electrodes to be cut within a range that would not be affected by the electric field. Compared to the original electrodes, the metal surface area has been reduced by approximately 40%.
- A series of holes are arranged orthogonally to the flow of radicals at the radical inlet. This prevents ions generated by the microwave discharge from being directly irradiated onto the electrode and allows a wide range of radicals to fill the cell.

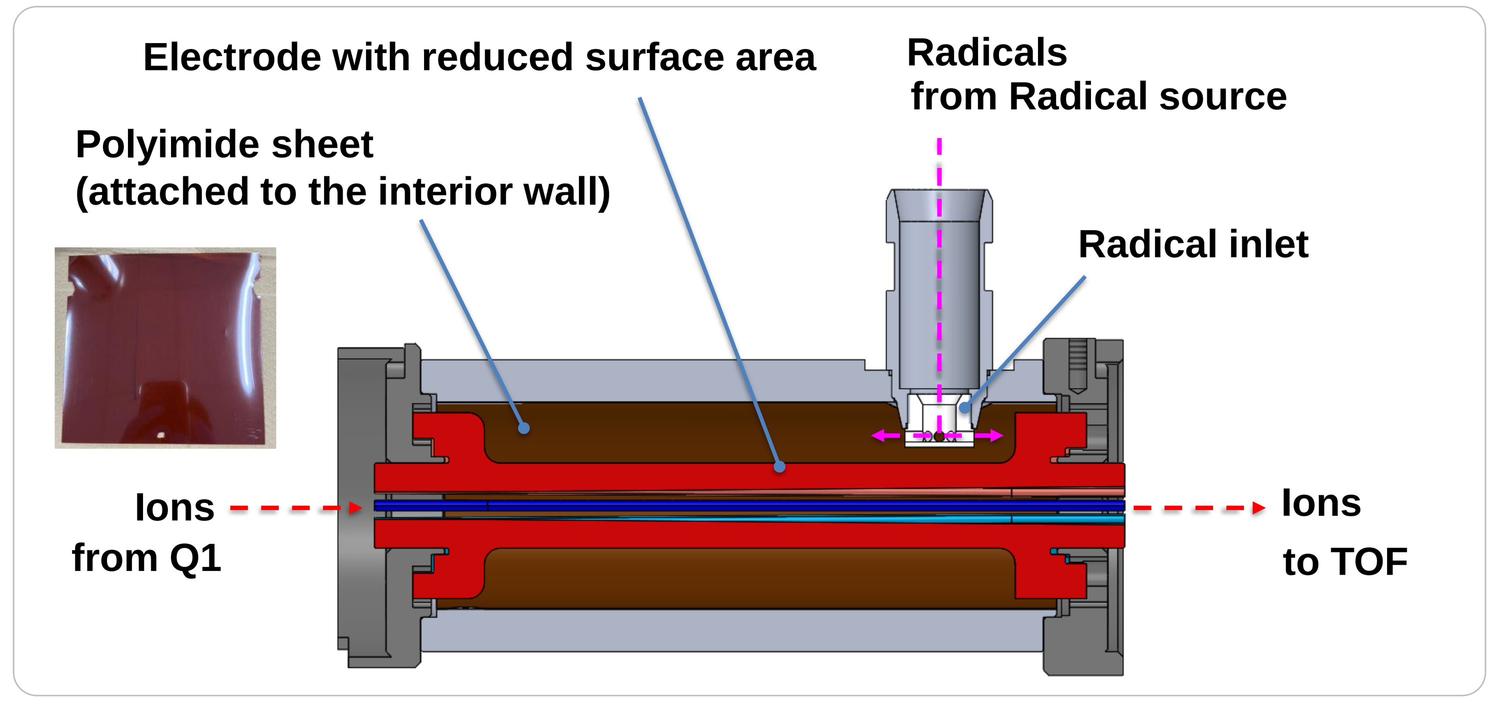

Fig. 4. Schematic diagram of the collision cell.

4. OAD MS/MS spectrum

- A model lipid PC (18:1) was used to compare the OAD efficiency of the conventional and newly developed systems. In OAD-MS/MS, OH• selectively oxidized and cleaved at C=C, which clearly provides C=C positional information for lipids.
- The data of the conventional system is obtained by Uchino.H[3], and the system had no polyimide sheet of the collision cell and no surface area reduction of the electrode.
- The ratio of the intensity of OAD-specific product ions to precursor ions was 0.29% for the conventional system and 7.9% for the newly developed system, indicating a significant increase in OAD efficiency.

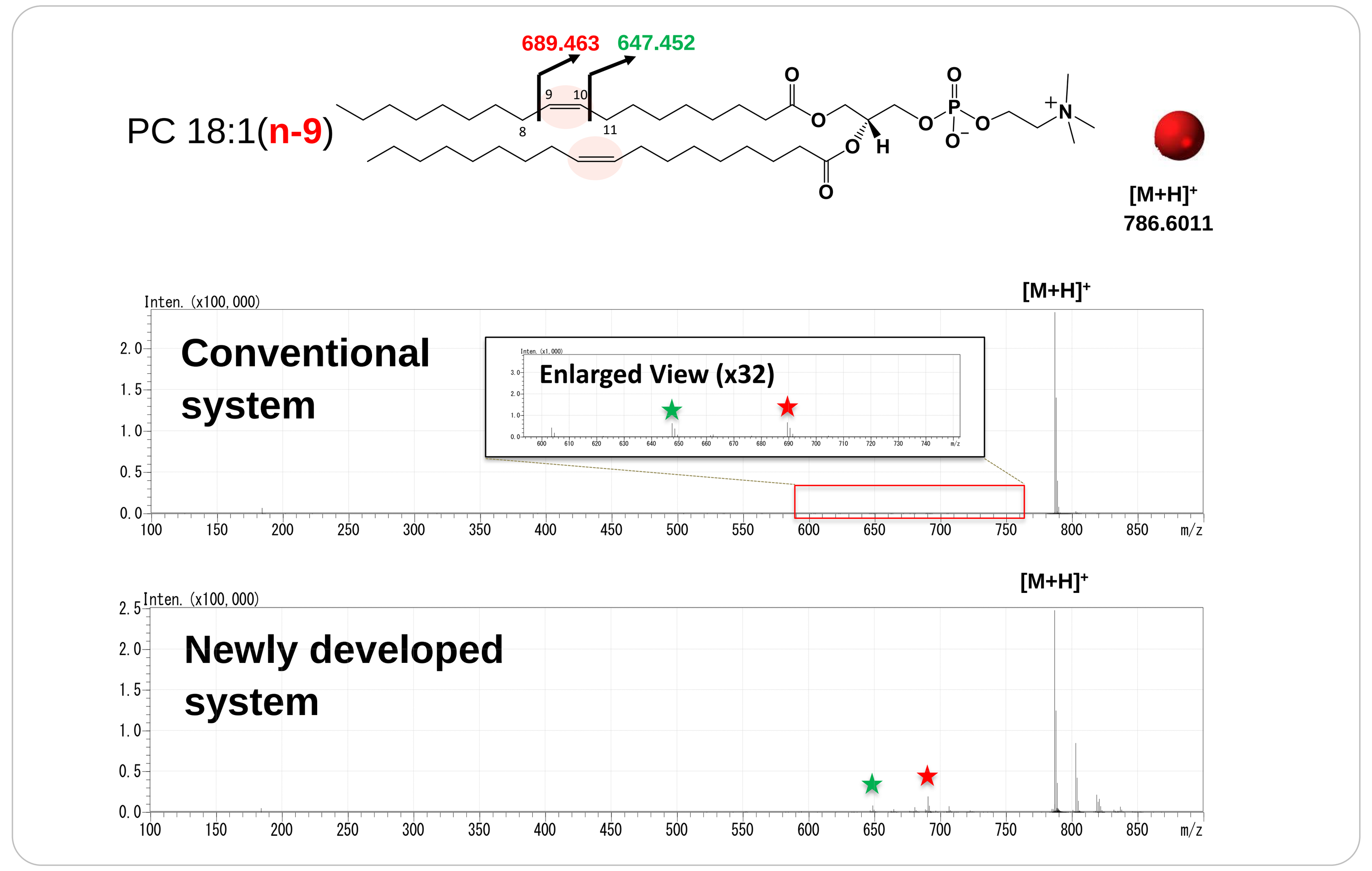

Fig. 5. OAD spectrum comparison of conventional and new systems.

5. Conclusion

- ✓ We successfully developed a collision cell that reduces radical recombination. As a result, the reaction efficiency of OAD in TOF-MS could be enhanced.
- ✓ The OAD-TOF system provides a powerful tool for obtaining structural information on compounds that cannot be obtained by CID.