博士学位論文審査要旨

２０２０年1月１４日

論 文 題 目：Comprehensive Study on the Low-energy Atomic Hydrogen Beam: From Production to Velocity Distribution Measurement
（低エネルギー原子源の包括的研究－生成から速度分布測定まで）

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要　　旨：

真空場を用いた質量分析による生体高分子の構造解析において、四重極イオントラップ部やコリジョンセル部に水素原子を導入し、水素原子付着・引き抜き反応を経由した解離反応(Hydrogen Attachment/Abstraction Dissociation: HAD)にもとづくパターン分析を行うことが有効であることが示された。しかし熱解離を用いる従来の水素原子生成法では、水素原子生成装置の寿命が十分でなく、安定な結果が得られないと言う問題があった。本研究では電子サイクロトロン共鳴現象に2.45 GHz のマイクロ波電力を結合させることにより、小型プラズマ源を設計・製作し、その原子源としての性能を評価している。論文では数種類の試作機をテストした上で、内径4 mm のアルミナ細管内に交流放電を励起する方式が、水素原子生成に対する性能が優れていることを示し、質量分析器に組み込んで評価を行うことにより、高い水素原子粒子束と寿命を確認している。

また、熱解離源との性能比較を行うことにより、高い閾値での水素付着が必要となる場合には高効率原子源の HAD に対する反応率が低下することを予測し、実験的に確認している。この現象を定量的に評価するため、専用の測定系を設計・製作し、原子源から放出される水素原子の速度分布を実測した。その結果、熱解離型原子源から得られる水素原子と比較して、マイクロ波原子源から生成される水素原子の温度が実効的に低いことを証明し、観測結果と比較している。

開発した原子源は水素プラズマのみでなく反応性プラズマの生成も可能であることを利用し、酸素ガスや水蒸気プラズマを安定に生成できることを実証した。特に水蒸気プラズマを生成することにより、水素原子とともに酸化水素 OH を効率よく生成することができるため、OH による脂質構造の解析に応用可能であることを実証した。この上で他のラジカルをプラズマ生成することにより、より広範囲な生体高分子分析も可能であることを提案・報告している。

本論文は、新規 2.45 GHz ECR 放電型原子源構造を提案した上で、その原子フラックス生成の基本原理としてプラズマ波動モードの遷移が関与していることを明らかにした。設計・製作した原子源の性能の高さと十分な寿命を実証するとともに、生体高分子質量分析法への新たな応用展開可能性を示している。よってその学術的価値は博士（工学）（同志社大学）の学位論文として十分高いものと認める。

総合試験結果の要旨

２０２０年１月１４日

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要　　旨：

本論文の提出者は同志社大学大学院理工学研究科電気電子工学専攻博士課程（前期課程）を2018年3月に修了し、2018年4月に本学理工学研究科電気電子工学専攻博士課程（後期課程）に入学し、現在、在籍中である。

本論文の内容の一部は、2件の米国物理学会国際会議抄録集（査読有）、1件のジャーナル論文に掲載され、既に十分な評価を得ている。2019年12月14日午後二時半より二時間に亘り、提出論文に関する博士論文公聴会が開かれた。講演後種々の質疑が行われたが、提出者の説明により十分な理解が得られた。公聴会終了後、審査委員による学力確認のための口頭試験を実施したところ、論文提出者の十分な学力を確認することができた。語学力については国際会議に第一著者として論文を提出して自ら発表を行っているのに加え、ニュージーランドの技術系企業と共同研究を行うなど、十分な能力を有すると判断した。以上、論文提出者の専門分野における学力、並びに語学力は十分であることを確認した。よって総合試験の結果は合格であると認める。

博 士 学 位 論 文 要 旨

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(低エネルギー原子源の包括的研究 - 生成から速度分布測定まで)

氏　　名： 島袋　祐次

要　　旨：

In this dissertation, the author opened and developed the new approach for fragmentation mass spectrometry in identifying the complex biomolecular structures. Unlike charged particles, electrically neutral atomic hydrogen can induce the fragmentation of massive biomolecules by the high reactivity without destroying fragile yet hydrogen insensitive bonding of functional groups. Two types of microwave driven compact radical beam sources which efficiently produce various kinds of reactive radicals were developed. The versatility of the radical source achieved realization of the peptide and lipid analyses. In order to understand the mechanism responsible for atom induced dissociation reactions, velocity distribution functions characterized by atomic temperature of hydrogen atoms produced in the two different radical sources have been measured by developing a dedicated atom velocity measurement system. The experimental results show a good agreement with calculated results of dissociation reaction for peptide molecules by density functional theory.

This study focused on the development of a new fragmentation technique to analyze the primary structures of unknown fragile biomolecules, especially in the post-translational modification (PTM) that characterizes the peptides. The PTMs have been believed to be the causes of several diseases, however, the structural analyses of the peptide ions including PTMs is considerably complicated due to their uncontrolled dissociation processes leading to different fragments. Although there are conventional ways to analyze a portion of the PTMs based upon the electron induced dissociation processes, the analyzable tar- gets are strictly limited since both incident electrons and analyzable targets have electrical charges. In order to resolve the problem of the existing methods, a new fragmentation technique, HAD (Hydrogen Attachment/Abstraction Dissociation), was proposed in 2016. In HAD method, electrically neutral atomic hydrogen works as a trigger of the peptide fragmentation preserving PTMs. In the original HAD study, a thermal cracking type atomic hydrogen source with a high temperature tungsten capillary injected atomic hydrogen to the reaction chamber. High temperature components of the source do not only cause outgassing, but also shortens the operational lifetime (~ 100 h) as tungsten becomes reactive against residual oxygen and halogens at an elevated temperature. Although the HAD experiment achieved the cleavage of the peptide ions, several prior researches could not induce the peptide fragmentation by atomic hydrogen injection. Thus, a wide energy range of the atomic hydrogen production is important for elucidation of the HAD mechanism.

A radio frequency (RF) plasma generator neither has high-temperature components nor has requirements to arrange complicated electrode structures to maintain high electric current necessary to run an ohmic heater in vacuum. The electrode structure of the RF source determines the discharge modes; the RF plasma are distinguished by plasma density into capacitively coupled plasma (CCP) and inductively coupled plasma (ICP). In general, RF plasma source utilize frequency in the MHz order to ignite and sustain a plasma. However, in this study, a 2.45 GHz microwave with a wavelength shorter than a typical MHz RF wave to reduce the operation gas pressure and increase the radical density. Microwave driven CCP and localized inductively coupled plasma (LICP) sources were developed in this study.

The development of the 1st and 2nd generation microwave driven CCP source indicated that the electrode geometry to enhance the local electric field was an important factor in drastically reducing the operating gas pressure. In contrast, the LICP type radical source that couples the input microwave power to the plasma by winding a coil around a small diameter dielectric tube adopted an electron cyclotron resonance (ECR) which significantly enhanced the ignition and stable production of the plasma. The modified 1.5th gen LICP source exhibited a high degree of dissociation of hydrogen compared with the CCP source. Though both microwave CCP and LICP source produced atomic hydrogen within the source plasma, microwave leakage and heat loss from the impedance matching circuit are not negligible because these dissipative factors induce the instability of the source operation.

In order to resolve these problems on the previous generation radical sources, tuner- integrated type microwave driven CCP and LICP sources were developed. Unlike the 2nd gen CCP source, the newly developed 3rd and 4th gen CCP sources were able to emit plasma efficiently as a form of a plasma plume. A copper plunger tunes the impedance of the source system easily without any external matching circuit. The 2nd gen LICP source is similarly tuned by the copper plunger which contacts the surface of the spiral antenna coiled around the dielectric tube. The developed 2nd gen LICP source exhibited three types of plasma excitation mode attributable to the field configuration, which is quite similar with the mode transitions well studied in the MHz-RF plasma sources. A velocity distribution function of produced atomic hydrogen in the developed sources have been measured by developing a dedicated mass separated time of flight (MSTOF) system. The atomic temperature of the 2nd gen hydrogen LICP was determined as 600 K by chi-square test regarding to the theoretical calculation. The atomic temperature of the 3rd gen CCP source was obtained to be ranging from 872 K to 1020 K for 40 W to 70 W power input. In contrast, hydrogen atoms produced in the thermal cracking source exhibited the two representative temperatures that can be attributable to the hot capillary and filament.

Demonstration of the HAD reaction with developed radical sources concluded that the cleavage of the peptide ions by atomic hydrogen injection requires a threshold energy for a hydrogen atom to induce the fragmentation. The 2nd gen hydrogen LICP injection did not show any fragmentation. However, the 3rd gen CCP and 1.5th gen LICP showed fragment ions similar to the original HAD product ions. Therefore, the atomic temperature generated in the 1.5th gen LICP source can be considered higher than that of the 2nd gen LICP source and lower than that of the thermal cracking cell.

The developed sources of three different energy ranges are applied as a probe of the negative hydrogen ion surface production at the cesiated low work function surface. The hydrogen atoms emitted from the thermal cracking source and the 3rd gen CCP source achieved conversion from an atomic hydrogen to the negative hydrogen ion at the surface. These phenomena also identical with the relationship in the temperatures obtained in the previous chapters.

A series of experiments have identified the characteristic of each radical source behavior for the three types of developed sources. The versatile tuner-integrated microwave driven sources can produce various kinds of reactive radicals without the need for pre- liminary impedance matching. The difference in temperature or the velocity distribution functions of three types of radical sources may open a new field of study in the fragmentation mass spectrometry utilizing radical induced dissociation.