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論　文　名　：Analysis of Pesticides by Gas Chromatography/Multiphoton Ionization/Time-of-flight Mass Spectrometry Using a Femtosecond Laser
（ガスクロマトグラフィー/フェムト秒レーザー多光子イオン化飛行時間型質量分析法による農薬の分析）

区　　分：甲

論文内容の要旨

In this dissertation, I have developed a new analytical method for trace analysis of pesticides, which is based on gas chromatography combined with multiphoton ionization time-of-flight mass spectrometry using a femtosecond laser tunable from the deep-ultraviolet (200 nm) to the near-infrared (800 nm) region.

In Chapter 1, a history of developing pesticides is briefly summarized and is introduced to the readers in the beginning of this chapter. The positive and negative sides of the pesticides to human being has been described for better understanding of the function of the pesticides. The definition of "pesticide" by the Food and Agriculture Organization is provided for the readers involved in the other academic fields different from the agriculture. A figure indicating the world pesticide demand has shown rapid production rates in the developing countries in Asia, Africa, and Central & South America. "*Silent Spring*", a famous book published in 1962 reports environmental pollution by wide-spread DDT (dichloro diphenyl trichloroethane). Since then, many scientists are more concentrating their attentions for solving the environmental issues. The pesticides can be classified according to the chemical structures and also by the killing targets to realize their functions. To assess the environmental pollution, it is necessary to measure the pesticides in the soil, surface water, atmosphere in the environment. Gas chromatography combined with mass spectrometry (GC/MS) has been utilized as one of the successful techniques. This analytical method is briefly summarized for understanding the state-of-the-art technologies for trace analysis of pesticides. As described, there are several ionization techniques in mass spectrometry, e.g., electron and chemical ionizations. Among them, a laser ionization technique using a tunable femtosecond laser provides an excellent tool for ionization of various pesticides. The research subjects explained in the following chapters are briefly introduced at the end of this chapter.

In Chapter 2, one of the most popular pesticides, hexachlorocyclohexane, is measured in this chapter. Structural and enantiometric isomers were separated by a GC column with a chiral stationary phase. Then, far-ultraviolet (200 nm) and deep-ultraviolet (267 nm) femtosecond lasers were used as the ionization source in multiphoton ionization MS. The elution order of the enantiomers, i.e., (+)-α-HCH and (-)-α-HCH, observed in the experiment was compared with the data predicted from the stabilization energies of the complexes and permethylated γ-cyclodextrin used as a stationary phase of the capillary column. When a

far-ultraviolet laser emitting at 200 nm was employed, resonance-enhanced two-photon ionization (RE2PI) was found to be a major process for these compounds. The molecular ions of HCHs were clearly observed, although the fragment ions dominantly appeared in the mass spectrum. The experimental data, which was unpredicted from quantum chemical calculation, was explained by efficient dissociation of a molecular ion. The result achieved in this study suggests that the analytical instrument used herein has a potential advantage for the determination of the pesticides with structural and enantiometric isomers in the environment and their elution order can be predicted from the data obtained by quantum chemical calculation.

In Chapter 3, three different types of femtosecond lasers emitting at 267 nm (ultraviolet), 400 nm (visible) and 800 nm (near-infrared) were used as the ionization source. A standard sample mixture containing 51 pesticides is measured using GC/MS using femtosecond laser ionization source. A two-dimensional display of GC/MS was successfully used for multi-component analysis of these compounds. Further investigations have been conducted at two laser wavelengths, i.e., 267 nm and 800 nm, to find optimal conditions for trace analysis and to find new rules to explain the efficiency of ionization. The data were compared with those obtained using quantum chemical calculations, in which numerous spectrometric properties such as the excitation and ionization energies and the absorption spectrum and the oscillator strengths were calculated for the neutral and ionized species. As a result, several additional rules were found for explanation of the observed data. The sample of pesticides in the homogenized matrix obtained from kabosu and other vegetables were measured and the constituents were clearly separated and identified in the data, suggesting excellent performance of the analytical instrument for practical trace analysis of the multi-residue of pesticides in the environment.

In Chapter 4, all the studies in this dissertation are summarized in this chapter.