

# Laser ionization mass spectrometry for analysis of environmental pollutants

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## Abstract of Dissertation

Persistent organic pollutants (POPs) in the environment pose a serious threat to human health. Then, it is necessary to monitor the level of POPs in the environment. However, the methods currently used for this purpose have their pros and cons depending on the application. Accordingly, it is desirable to develop a sophisticated analytical method regarding both sensitivity and selectivity to measure POPs for environmental protection.

A sophisticated analytical method regarding both sensitivity and selectivity is required for the determination of persistent organic pollutants (POPs) in the environment. A technique of multiphoton ionization (MPI) has been developed for soft ionization in mass spectrometry (MS), providing a molecular ion and large fragment ions in many cases. Accordingly, this approach is favorable for the environmental analysis of various organic compounds. In this thesis, I developed an analytical method for trace analysis of POPs, which is based on a hyphenated technique of gas chromatography and time-of-flight mass spectrometry based on MPI (GC-MPI/TOFMS). The optimal condition for MPI was examined for two types of POPs, i.e., perfluorinated carboxylic acids (PFCAs) and nitrated polycyclic aromatic hydrocarbons (NPAHs). This dissertation is divided into four chapters as follows:

Chapter 1 is an overview of the introduction of POPs and analytical techniques related to this study. A variety of POPs are listed in the Stockholm Convention, which includes industrial waste materials and toxic organic compounds produced by combustion of fossil fuels. Analytical methods related to this study, e.g., MS and its significance when applied to trace analysis, are summarized in this chapter.

Chapter 2 reports on the trace analysis of PFOAs for solving an environmental issue. GC combined with electron ionization mass spectrometry (GC-EIMS) is one of the most commonly used techniques for measuring PFCAs. However, a molecular ion in EIMS is considerably weak, providing limited information on the molecular weight of the analyte. To solve this problem, a novel techniques based on GC-MPI/TOFMS was developed for soft ionization in this chapter. For analyzing PFCAs, the analytes

were measured after a derivatization reaction with two types of aromatic compounds containing a bromomethyl group, i.e., 2-(bromomethyl)naphthalene (BMN) and benzyl bromide (BB). The conditions for the reaction were examined in terms of reaction temperature and time and the concentration of the derivatizing reagent. At optimal conditions, the derivatized compounds of PFCAs-MN and PFCAs-B were measured by GC-MPI/TOFMS using an ultraviolet femtosecond laser (267 nm) as the ionization source. Due to superior separation of PFCAs-B by GC, BB was found to be successfully used as the derivatizing agent for measuring PFCAs. The other bromomethyl aromatic compounds were also evaluated as candidates for use as a derivatization reagent in the future.

Chapter 3 reports on the trace analysis of NPAHs, one of the POPs suspected as carcinogenic compounds contained in particulate matter 2.5 (PM<sub>2.5</sub>). These organic compounds are mainly determined by GC-EIMS. However, NPAH are rather dissociative, making the identification of the analytes in a complex sample mixture and obtaining the information of the molecular weight more difficult. Therefore, a novel technique is desirable for trace analysis of NPAHs. In this chapter, the efficiency of MPI and the ionization mechanism were investigated by GC-MPI/TOFMS using a femtosecond laser emitting at 343, 257, 206 nm, and a combination of 343 and 257 nm. Resonant two-photon ionization (RE2PI), resonant three-photon ionization (RE3PI), and nonresonant three-photon ionization (NR3PI) are possible schemes, depending on the wavelength of the laser used. A large signal of molecular ion was observed when a combination of 343 and 257 nm was employed. This favorable result would arise from small excess energy achieved using the 343-nm (3.61 eV) and 257-nm (4.82 eV) pulses, the sum energy (8.43 eV) of which was comparable to the ionization energy (7.36 – 10.45 eV) of these compounds. Thus, fragmentation was suppressed significantly, which was preferred for reconstruction of the chemical structure of the analyte. The present technique was found to provide superior performance for the trace analysis of NPAHs.

Chapter 4 presents a summary of this dissertation.