Chapter 1

Introduction

Since J.J. Thomson first succeeded in the mass separation of neon isotopes using magnetic and electric fields in 1912, various types of mass spectrometers have been invented and developed according to purposes specific to different research fields. From the 1920's to 1950's, mass spectrometers made great progress in the increasingly precise measurement of atomic mass. In recent years, mass spectrometers have become one of the most indispensable instruments to identify substances from their mass data in a wide variety of scientific research fields including vacuum technology, geology, chemistry, biology, medical science, environmental science, and so on. This widening of research fields requires mass spectrometers with their improved performances in their mass resolution, mass accuracy, mass range, and sensitivity. Their compact size and low investment cost have also been key factors for the application of mass spectrometers.

At present, mass spectrometers for which the theoretical principles and operating techniques are well-established can be classified into static and dynamic type mass spectrometers. The static type mass spectrometer employs static magnetic and electric sector fields. The mass separation is achieved by observing mass dispersion produced in the sector magnetic field. The time-of-flight mass spectrometer (TOF-MS) uses a static ion accelerating field. The measurement of ion velocities is equivalent to the mass spectroscopy. In contrast, the dynamic type spectrometer utilizes a time-varying electric field. An ion cyclotron resonance mass spectrometer (ICR-MS), a radiofrequency quadrupole mass filter (RF-QMF) and an ion trap mass spectrometer (ITMS) are categorized in the dynamic mass spectrometer. The selection of a specific mass in the dynamic mass spectrometers is based on the dynamical resonance of the characteristic oscillation of ions in a electric or magnetic field when a time-varying field is applied.

Among the dynamic mass spectrometers, RF-QMF and ITMS are very attractive, since they are very compact and inexpensive. However, the performance of these rather new spectrometers is, at present, inferior to those of other mass spectrometers. In RF-QMF and ITMS, the performance items such as mass resolution, mass accuracy and sensitivity are related to several factors. The three-dimensional shape of electrodes in the actual RF-QMF is usually approximated by four rods with circular cross sections. Machining of the ring and end-cap electrodes in the actual ITMS is difficult. The approximation or distortion of the shape of the electrodes from their theoretical shape gives rise to higher order terms in the ion focusing or trapping fields, which yields some aberrations. Even a small positioning error in the mechanical construction of the electrodes will also contribute to production of aberrations. Voltages applied to the electrodes involve a certain amount of ripples and instability. The time rate (speed) or mode of mass scanning in a mass range must be optimized to obtain higher performance. The pressure of the ion buffering gas in ITMS and the injection method of ions into ITMS must be optimized to obtain reasonable sensitivity.

Prior to the present work, several authors developed theoretical methods to examine how the above factors limited the performance of RF-QMF. In early studies, Dawson and Whetten[1] calculated ion trajectory basically by numerical integration of the fundamental equation, *i.e.* the Mathieu equation. Richards *et al.*[2] employed the matrix method to obtain the position and velocity of an ion at a point of the RF phase ξ by calculating the state transition matrix from ion's initial conditions. Baril and Septier[3] proposed calculation of ion trajectories by phase-space dynamics using the matrix method to evaluate the entrance conditions for ions to transit

RF-QMF successfully. The effects of displacing the rod electrode and using the round rods were considered by Dawson and Whetten[4]. All of these development, however, were based on the analysis of ion trajectories in the two-dimensional electric quadrupole field in the plane perpendicular to the four rod electrodes. Approximation of the hyperbolic shape of the electrodes by circularly shaped ones and the fringing fields at the entrance and the exit of the four rod electrodes are known to influence the performance of mass spectroscopy with RF-QMF. In order to evaluate these factors quantitatively, a simulation method is required to calculate ion trajectories in a three-dimensional electric field.

With regard to ITMS, the first application of numerical methods to analysis of a single ion trajectory in the quadrupole ion trap was reported by Dawson and Whetten[5]. At that time, the ion trap applications were limited to use as a storage device for specific ions, not as a mass spectrometer. Since the ion trap has been developed as a mass spectrometer, *i.e.* ITMS, the numerical methods have also been improved. March *et al.*[6] provided a computer program SPQR especially to simulate an ion trajectory in a supplementary quadrupole, or dipole resonance field[7] by a field interpolation method. The ion trap simulation program, ITSIM, proposed by Julian *et al.*[8] was developed to great success. Its features permit simulation of external ion injection, bath gas damping, and resonance excitation. In both SPQR and ITSIM the electric fields are calculated by adding supplementary fields to the ideal quadrupole one. On the other hand, the ion simulation program SIMION, which was well-established by Dahl[9], supports ion simulation in the ion optics by calculating the three dimensional electric field formed between the actual shaped electrodes. SIMION is a multipurpose program suitable for simulating ions in various kinds of ion optics such as ion detection and lens systems, ITMS, RF-QMF and so on. However, it does not provide ion simulation during mass scan, which is a specific need for RF-QMF and ITMS, because ion simulation by calculating the actual electric field requires a lot of computational time.

Recent progress in computers has opened up a new possibility for calculation of electromagnetic fields numerically under the boundary conditions of a realistic electrode configuration in actual spectrometers. In the present investigation, therefore, a computer program has been developed to simulate the motions of ions in RF-QMF and ITMS[10]. It is named PISA-QMS, being abbreviated from Program for Ion trajectory Simulation Analysis in Quadrupole Mass Spectrometers. This program provides a simulation of the motions of ions during any process in a mass spectroscopy, *i.e.* injecting ions, scanning to obtain a mass spectrum, and ejecting ions. The calculation of three-dimensional electric fields can be carried out for realistically shaped electrodes. The positioning error of the electrodes in the mechanical construction and the effect of buffering gas and space charge can also be included in PISA-QMS.

The application of our new program PISA-QMS to problems in RF-QMF and ITMS has revealed several new aspects of the correlations between performance and related factors. In particular, the following three results are significant for confirming that PISA-QMS is a powerful tool for the optimal design and operation of RF-QMF and ITMS.

(1) Transmission through RF-QMF.

In this investigation, ion trajectories injected into RF-QMF have been simulated. We carefully examined the dependence of the ion transmission efficiency on the focal position of ions at the QMF entrance. The optimum region of the focal position to enhance the transmission efficiency was found. In the case that ions are injected with higher energy of 100-200eV and decelerated at the entrance part, the mechanism how the transmission efficiency is determined was clarified.

(2) Ion trapping efficiencies in ITMS.

From calculation of the trajectories of ions injected into ITMS, we have proved for the first time that the addition of the second and third dominant oscillation modes to the fundamental oscillation mode plays a crucial role in describing the motions of ions injected into ITMS. The new approximate function consisting of the superposition of the three oscillation modes, is remarkably enhances understanding of the dependence of the ion trapping efficiency on RF phase, RF voltages and ion injection energies. Based on the simulation results, the optimum values of RF voltage and ion injection energy to improve the ion trapping efficiencies were clarified. Furthermore, a new injection method to solve the problem of the uneven sensitivity among different ion species was derived.

(3) Method of mass scanning in ITMS.

Mass spectra have been simulated by calculating the ion motions during conventional mass scanning in which the scanning speed is kept constant. When the mass scanning speed is set very low, the calculated mass resolution has been enhanced. The slow mass scanning meets with the two problems, scanning time expansion and shifting of the mass peak position, *i.e.* mass-shift. Through simulations in several cases with various scan speeds, we clarified the relationship between the scan speed and the ITMS performance items such as mass resolution and mass accuracy. Based on this relationship, a new scanning method, in which the scan speed is varied according to the ion mass, is proposed for the first time. The new scanning method was proved to achieve high resolution without mass shift or scanning time expansion by simulations.

The following part of this dissertation is arranged as follows. In Chapter 2, the principles of typical existing mass spectrometers are described for comparison of the concept of each type of spectrometer. In Chapter 3, the basic theory of ion motions in RF-QMF and ITMS is developed.

In Chapter 4, detailed discussions on the method of development of our computer program PISA-QMS are given. Calculation of the three-dimensional electric field, the trace of ion trajectories, and the models of interactions of ions with other particles (ion buffering gas and other ions) are described. Comparisons of the results obtained with PISA-QMS with other works are made to confirm the advantages of PISA-QMS from experimental and theoretical view points. In Chapter 5, the three results mentioned above are discussed. Finally, the present investigation is summarized in Chapter 6.