Inorganic Mass Spectrometry

Principles and Applications

JOHANNA SABINE BECKER

Research Centre Jülich, Germany

John Wiley & Sons, Ltd

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Anniversary Logo Design: Richard J. Pacifico

Library of Congress Cataloging-in-Publication Data

Becker, Johanna Sabine.
Inorganic mass spectrometry : principles and applications / Johanna Sabine Becker.
p. cm.
Includes bibliographical references.
ISBN 978-0-470-01200-0 (cloth : acid-free paper)
1. Mass spectrometry. 2. Chemistry, Inorganic. I. Title.
QD96.M3B38 2007
543′.65—dc22 2007018922

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 978-0-470-01200-0

Typeset in 9/11pt Times by Integra Software Services Pvt. Ltd, Pondicherry, India
Printed and bound in Singapore by Markono Print Media Pte Ltd, Singapore
This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

For my parents

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Foreword

Inorganic mass spectrometry (inorganic MS) has had an important presence in chemical analysis for many years and much has been written, especially since the adoption of inductively coupled plasma mass spectrometry, ICPMS, on a routine basis. Hence the clear need for a comprehensive look at this field in a manner readily understandable with benefit for novice or expert. Dr J. Sabine Becker has risen to this challenge and produced an excellent book that gives a unique perspective through its broad coverage of the field by reviewing the important aspects of it, as we know it today. The reader will find excellent coverage of sample preparation, sample introduction, ion sources, ion separation, ion detection and an extensive illustration of applications. It is further strengthened by the exceptionally high number of references. The writing is clear and concise and even the novice can come to a working level in the subject without having to search external references, or having to wade through heavy mathematical arguments. A very important plus with this offering is that it is a one-author book and offers a coherence of thought and style that no multi-authored work can achieve. Thus as one progresses through Dr Becker's chapters, it is more like moving through a good textbook than a series of review chapters. Beyond major libraries, this offering is well suited for a graduate course in inorganic mass spectrometry.

The introductory chapter is brief but provides an ample introduction to mass spectrometry and leaves one comfortable as he/she moves on to the historical and instrumentation chapters that follow. A few of the basic equations are given as part of the review of basic concepts. In these few pages Dr Becker clearly introduces the concepts of atomic mass units relative to carbon, isotopes and isotope abundance. Figures 1.1 and 1.2 go hand in hand in providing the reader with the three major parts of a mass spectrometer (source, ion separation, detection) and show various alternatives for each of these. The subtle use of color in these and subsequent figures adds an attractive benefit for the reader.

Chapter 1 goes into some nicely done historical detail. This chapter begins in the late 19th century and traces those developments through the years. The numerous figures and pictures show well some of the early ingenuity of those exceptional scientists and Dr Becker is careful to note the importance assigned to mass spectrometry by the scientific community of that time; one measure being the numerous Nobel prizes awarded. The history as she presents it provides an excellent context for the future and current developments that this work highlights. Of particular interest to this reader are the early discussions about Wien, Aston and Thompson.

Chapter 2 highlights ion sources for inorganic mass spectrometry and given its popularity, it is no surprise that the inductively coupled plasma (ICP) receives the most attention. Noteworthy here are Figures 2.1 and 2.2, which provide informative summaries regarding atomization and ionization processes leading to the atomic ion followed by an excellent discussion of the ICP highlighting its operation and discussing solution nebulization for sample introduction. The reader will also find optimization discussion and figures – for example, fraction of ionization in the plasma. After the primary discussion of the ICP as an ion source, Figure 2.12 summarizes the various sample introduction modes associated with the ICP and does so in an easily visualized fashion. Dr Becker continues with discussions on selected sample introduction methods to the ICP including laser ablation, electrothermal vaporization, and hydride generation. This is followed by other sources; namely, spark ion source, laser ion source, glow discharge ion source, thermal surface ion source (TIMS – Figure 2.28 shows elements available), SIMS, and SNMS. Following these, softer ion sources for fragmentation and molecular ion formation; namely, electron ionization, MALDI and ESI are briefly discussed. Table 2.2 provides an excellent comparative summary of the various ion sources.

Chapter 3 continues Dr Becker's excellent presentation and has ion separation as its focus. The chapter begins with well developed text on electric and magnetic field sectors for ion separation and culminates with the combination of both sectors – double focusing ion separation as the most important of the three sector possibilities for high resolution inorganic mass spectrometry. However, the quadrupole mass filter is clearly the most widely used and often sold commercially available ion separation system and therefore, appears prominently in the text. This is followed by the time-of-flight (TOF), which has the ability to take spectra very fast and therefore should be highly amenable to laser ablation, chromatography and other sample introduction methods where a transient sample pulse passes through the ion separator. Two other ion separation methods are discussed in this chapter; ion-trap technology and FTICR (fast Fourier transform ion cyclotron resonance), although these are most widely used for molecular MS. The last part of the chapter reviews the concepts of resolution and abundance sensitivity – important to ICPMS users for any of the three commercially available inorganic MS types.

Chapter 4. Ion detectors are the last of the three major mass spectrometer components. With a particular focus on inorganic MS, a concise and well-written chapter results. Dr Becker begins with a discussion of the classical Faraday cup detector, which in its current configurations are still in use today. The secondary electron multiplier (SEM) is introduced and the explanation is readily understandable to the novice through a carefully designed Figure 4.2. It becomes apparent the electron multiplication is the best choice for low-level signals. She draws attention to the SEM in the dual ion mode for either the analog or pulse counting. For extended dynamic range the combination of Faraday cup and SEM is discussed with high ion current channeled to the Faraday detector and low ion currents to the SEM. The channel electron multiplier (CEM or channeltron) and microchannel plates are the next topics. The CEM is shown in Figure 4.5 in both the analog and pulse counting mode. As a modern alternative to the Faraday cup is the Daly detector (Fig. 4.6). This short chapter finishes with multi-collector devices for true simultaneous multi-element analyses.

When ion sources, ion separation and detection are combined, a mass spectrometer system results. While some choose to build their own, a wide variety of these are commercially available, offering as wide a combination of sources, separation means and detection. Chapter 5 focuses on these systems and is given the general title of "Instrumentation." For inorganic MS, Figure 5.1 and 5.2 illustrate some possible combinations by adding sample introduction to ion sources and separation (the detector is implied). Initially the discussion involves the quadrupole as the ion selector, since it is the most widely used with ICPMS. Collision/reaction cells are also brought into the discussion highlighting the additional power ICPMS has for detection through non-metal and some metal ions. Table 5.1 compares four different ICPMS quadrupole products. The plasma source ion trap is also discussed followed by ion separation using a double focusing sector field instrument with a single detector. Time-of-flight instrumentation is then carefully reviewed and Figure 5.10 illustrates a recent market introduction. Multi-detector (named multicollector) sector field instruments make up the next portion of the chapter and figures of merit for sector field instruments are compared in Table 5.2. Solution sample introduction via nebulization, hydride generation and flow injection are the next topics plus hyphenated methods are touched on here. As an important topic, Laser Ablation ICPMS is included in Chapter 5. At this point Dr Becker departs from ICPMS as the source to a number of other inorganic MS systems, of which Glow Discharge may be the most important today. Overall the discussion provides an excellent overview of the types of instrumentation useful for inorganic mass spectrometry.

Chapter 6 begins the discussion on analytical and practical considerations regarding the use of inorganic MS. Qualitative use of the techniques point out salient issues that need to be considered such as isotope pattern, mass determination and interference problems, which are well illustrated in the accompanying figures. Lengthy discussion is given to quantitative approaches and, as might be expected, internal standards, standard addition and isotope dilution get a lot of attention. Although not in method detail, the analyst can benefit highly from the discussion, which presents good “how to” ideas. Beyond solution sample introduction follows laser ablation for solids. An important focus here is the topic of calibration for quantitative determination by laser ablation. Next the reader will find an often ignored or minimized aspect of the analysis – sample preparation. The chapter is easy reading, but of high importance.

Gaseous and volatile compound analysis is covered in Chapter 7. Since all MS systems ultimately require gas phase ions, such a topic is of high importance in inorganic as well as molecular MS analysis. The chapter is short, yet does cover sample preparation for volatiles as well as some important applications. This chapter is very well referenced.

Chapter 8 addresses one of the most important features of inorganic MS – isotope ratio or isotope abundance measurements. As part of a brief introduction, Figure 8.1 provides a good departure for applications of isotope ratio measurements. The discussion provides insights to the capabilities of inorganic MS for isotope ratio measurements, mass discrimination effects, isotope ratio measurements by various types of MS. Table 8.4 gives some interesting applications of isotope ratio measurements. Multicollector ICPMS is discussed for precise isotope ratios and this section is followed by isotope dilution measurements. The chapter concludes with a focus on long-lived radionuclides, geochemistry and geochronology. As is Dr Becker’s pattern, the reference section is very well done.

Chapter 9 is a major offering in fields of inorganic MS. At 205 pages, it details applications of inorganic MS for trace, ultratrace and surface analysis. Indeed, no forward can do justice to this exceptional review of applied inorganic MS, nor with space limitations adequately describe it. Notable however, is the richness of figures and tables drawing together from many resources comparative information along and across the various inorganic MS methods and their unique strengths and weaknesses. In fact, the reader will find 46 tables, 67 figures and 12 reference sections included in Chapter 9. The various MS methods and their numerous applications to a variety of sample types require an exhaustive search and clearly this was done for this book chapter (e.g. Ref. Section I alone has 159 references). Applications include materials science, environmental science and control, biology, bioengineering, medicine, foods, geology and geochemistry, cosmochemistry and space science, long lived radionuclides, forensic applications, and additional further applications. Dr Becker also devotes a section of this chapter to a very important aspect of inorganic MS, polyatomic ion formation. All-in-all this chapter provides either the novice or expert an excellent overview on up-to date applications of these powerful MS techniques.

Chapter 10 briefly addresses future trends as Dr Becker sees them emerging. She looks to higher resolution mass spectrometers for better interference separation, better sensitivity and lower detection limits. With this enhanced analytical power she also predicts increased user friendliness, better isotope ratio measurements, smaller sample sizes, enhanced capability to handle transient signals and further advances in sample introduction.

Ultimately the reader will find this work an excellent addition to their library. As earlier indicated, the text reads well, is crisp and concise and provides excellent up-to-date coverage of inorganic mass spectrometry and the important ancillary topics.

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Preface

For many decades mass spectrometry has occupied an outstanding position among analytical techniques due to its universality and it has covered wide fields of application in atomic physics (determination of exact masses of isotopes, half-lives of radionuclides or of isotope abundances), chemical reaction analysis in ion molecular chemistry, studies of the kinetics of chemical processes and determination of thermodynamic data. It should be noted that no other analytical method has had such a significant influence and huge impact in so many fields of modern science and technology as mass spectrometry. Starting with a historical overview of mass spectrometry, this book presents the fundamentals and instrumentation of the most important inorganic mass spectrometric techniques, describes a wide range of analytical methods and a multitude of applications in materials, biological, geological and environmental research including recent developments in combination with biomolecular mass spectrometry for the special field of proteomics – discussed as metallomics and phosphoproteomics – with fascinating applications in medicine, biology and the life sciences. Of all the inorganic mass spectrometric techniques, inductively coupled plasma mass spectrometry (ICP-MS) has a leading place resulting in an exponential proliferation of exciting research and publications. The field of ultratrace and isotope analysis itself has been undergoing continuous development especially in combination with off-line or on-line trace matrix separation. On-line techniques such as HPLC-(high performance liquid chromatography) or CE (capillary electrophoresis)-ICP-MS have been developed as hyphenated techniques in order to reduce isobaric interferences and matrix effects, to facilitate speciation analysis and to improve their limits of detection of elements.

In the first part of the book, fundamentals of inorganic mass spectrometry (basic principles and developments of ion sources, ion separation systems and ion detectors) and instrumental developments in ICP-MS, LA(laser ablation)-ICP-MS, GDMS (glow discharge mass spectrometry), SIMS (secondary ion mass spectrometry), TIMS (thermal ionization mass spectrometry) and other techniques are described. The second part focuses on a multitude of quite different applications in materials science, environmental science and technology, biology and medicine, bioengineering, food analysis, geology and geochemistry, radioanalytical or forensic applications and cluster research.

This book ‘Inorganic Mass Spectrometry: Principles and Applications’ will give an insight into the state-of-the-art in mass spectrometry in different challenging tasks and recent developments and will present representative coverage of many fields of different topics. It is concerned with the theoretical and experimental conditions of different types of mass spectrometers and gives an overview of new methodological developments and trends for analytical work and modern applications, especially in survey, trace, ultratrace, surface (micro- and nanolocal analysis, imaging and depth profiling) and isotope analysis.

In the text the recommendations made from the International Union of Pure and Applied Chemistry (IUPAC), the International Union of Pure and Applied Physics (IUPAP) in respect to definitions (terms), symbols, quantities together with the International System of Units (SI) in respect to symbols in physical chemistry are considered.[1]

This book is the result of more than 30 years intensive research, experience and routine work in nearly all the fields of inorganic mass spectrometry described here and provides scientists, researchers, engineers and graduate students in analytical chemistry with a basic knowledge of the many facets and recent trends and applications of this important field of mass spectrometry.

Johanna Sabine Becker

Reference

1. Mills, I., Cvitas, T., Homann, K. *et al., Quantities, Units and Symbols in Physical Chemistry (IUPAC: Green Book)*, Blackwell Science, Oxford (1998).

Acknowledgements

I was first introduced to mass spectrometry after I had completed my PhD in quantum chemistry in 1974 when I was working as a young scientist under the supervision of H. J. Dietze at the Institute of Stable Isotopes (German Academy of Sciences, Leipzig) studying the wide field of stability and instability of isotopes in nature. My first research in mass spectrometry concerned investigations of the double-β decay of ^{96}Zr to ^{96}Mo in Precambrian zircon samples from the Baltic Shield via a precise isotope analysis of molybdenum using thermal ionization mass spectrometry (TIMS). At that time, the precision of mass spectrometers with single ion collection was not sufficient to measure very small isotope variations of molybdenum.

During my research in Leipzig I developed and applied analytical methods for the precise isotope analysis and determination (using the isotope dilution technique) of concentrations of U, Rb, Sr, Nd and Sm for age dating of geological samples from the Ore Mountains in Germany by TIMS. In addition, multi-element analytical techniques for the determination of trace elements on solid samples (geological samples, high-purity materials, ceramics, biological materials) by spark source mass spectrometry (SSMS) and laser ionization mass spectrometry (LIMS) were developed and applied. Furthermore, the design and construction of new types of laser ion sources, basic investigation on the formation of molecular, cluster and atomic ions in laser and spark plasma, and the development of ultrasensitive mass spectrometry (within the framework of cooperation with the Nuclear Research Centre in Dubna, Russia) were steps leading to advances in inorganic mass spectrometry. Mass spectrometric research into laser ablation and plasma deposition processes was also pursued during our work on the laser-induced plasma deposition of thin films, e.g., BN and C layers, W–C multiple layers and thin superconducting films, first in the ultrahigh vacuum ion source of the mass spectrometer and later in the deposition chambers developed for the preparation of superconducting thin layers.

For most of my career I have worked in the Central Division of Analytical Chemistry at the Research Centre Jülich – since 1992 as Head of Mass Spectrometry. In this time I have been concerned with the development and application of inorganic mass spectrometric techniques (such as ICP-MS, LA-ICP-MS, SSMS, LIMS, GDMS, SIMS and SMNS) for trace, ultratrace, isotope and surface analysis in environmental, biological and materials research, in the life sciences,

medicine, bioengineering and geological research. Other major research topics are the ultrasensitive determination of long-lived radionuclides in the environment and the development of advanced mass spectrometric techniques for micro- and nanolocal analysis in medicine and the life sciences, e.g., for the quantitative imaging of elements in thin sections of brain tissue (imaging mass spectrometry) and for the analysis of separated metal-containing proteins in 2D gels (metallomics and phosphoproteomics) in combination with biomolecular mass spectrometry. It would not have been possible to explore this huge area of work in inorganic mass spectrometry without fruitful cooperations with the departments at the Research Centre Jülich and also with national and international scientists.

First of all, I would like to express my deepest and warmest thanks to my teacher in the field of mass spectrometry, H. J. Dietze (former head of the Central Department of Analytical Chemistry, Research Centre Juelich). I am greatly indebted to him for stimulating my interest in mass spectrometry, for our very successful scientific cooperation in inorganic mass spectrometry over a period of more than 25 years, and also for his motivation and continuous support in encouraging me to write such a comprehensive book on inorganic mass spectrometry, for countless helpful and fruitful discussions, valuable advice and critical reviews.

I am grateful to all my students, postdoctoral fellows and associates from Germany, USA, France, Israel, Italy, Russia, Belarus, Ukraine, Poland, Egypt and India, who studied at my laboratory and contributed to the experimental development of analytical techniques in inorganic mass spectrometry during my scientific career at the Research Centre Jülich. I am indebted to many scientists worldwide for numerous fruitful discussions accelerating analytical progress in mass spectrometry in the last decade.

I would like to thank J. Carter-Sigglow (Jülich) for a critical revision of the language and J. Cossham as the Publishing Editor from John Wiley & Sons, Ltd for her support and fruitful cooperation.

Last, but not least, I wish to thank my family for their great support, especially my daughter, J. Susanne Becker, for joining me in a new and interesting cooperation on metal-, phosphorus- and selenium-containing proteins (metallo-, phospho- and selenoproteomics) using a combination of LA-ICP-MS and MALDI-MS.

Introduction to Mass Spectrometry

Mass spectrometry is one of the most important analytical techniques used today for the determination of element concentrations especially in the trace and ultratrace range, for surface and isotope analysis, and for the structural analysis of organic and bioorganic compounds, due to its very high sensitivity, low detection limits and the possibility of analyzing very small sample volumes.

Mass spectrometry is based on the physical properties of the atomic nucleus. The atomic nucleus of any chemical element consists of protons and neutrons. In an electrically neutral atom the number of positively charged protons in the nucleus equals the number of negatively charged electrons in the shells. The number of protons (Z = atomic number) determines the chemical properties and the place of the element in the periodic table of the elements. The atomic number Z of a chemical element is given as a subscript preceding the elemental symbol (e.g., ${}_{1}\mathrm{H}$, ${}_{6}\mathrm{C}$, ${}_{17}\mathrm{Cl}$, ${}_{26}\mathrm{Fe}$ or ${}_{92}\mathrm{U}$). Besides the protons, uncharged neutrons with nearly the same mass in comparison to the protons ($\mathrm{m_n} = 1.67493 \times 10^{-27}\,\mathrm{kg}$ versus $\mathrm{m_p} = 1.67262 \times 10^{-27}\,\mathrm{kg}$) stabilize the positive atomic nucleus. In contrast to the mass of the protons and neutrons in the nucleus, the mass of the electrons is relatively small at $\mathrm{m_e} = 9.10939 \times 10^{-31}\,\mathrm{kg}$.

The number of nucleons is equal to the sum of the number of protons (Z = atomic number) and number of neutrons (N) in the nucleus and is defined as the mass number (A = nucleon number)

$$A = Z + N \tag{1}$$

The mass number A of an isotope is given as a superscript preceding the elemental symbol (e.g., ${}^{1}\mathrm{H}$, ${}^{12}\mathrm{C}$, ${}^{35}\mathrm{Cl}$, ${}^{56}\mathrm{Fe}$ or ${}^{238}\mathrm{U}$).

Isotopes of a chemical element are nuclides with the same number of protons (Z) but a different number of neutrons (N) in the atomic nucleus. Isotopes of a chemical element (e.g., ${}^{1}\mathrm{H}$ and ${}^{2}\mathrm{H}$ of hydrogen; ${}^{35}\mathrm{Cl}$ and ${}^{37}\mathrm{Cl}$ of chlorine or ${}^{54}\mathrm{Fe}$, ${}^{56}\mathrm{Fe}$, ${}^{57}\mathrm{Fe}$ and ${}^{58}\mathrm{Fe}$ of iron, respectively) have the same number of protons (Z) and possess the same chemical properties, but differ in the number of neutrons (N) and thus in the mass number (A). With increasing Z, the number of neutrons in a stable atomic nucleus is higher than the number of protons. For mono-isotopic elements,

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which possess only one stable isotope with an abundance of 100 %, the mass of the isotope is than equal to the atomic weight. Twenty chemical elements in the periodic table are mono-isotopic. Twenty-one chemical elements have two stable isotopes (di-isotopic elements), respectively. Seven relatively light elements consist of three stable isotopes. For the majority of chemical elements more than three stable isotopes (poly-isotopic elements) exist. The isotopic composition of elements is demonstrated in the mass spectrum, which is the 2D representation of measured ion intensities in dependence of the mass-to-charge (m/z) ratio ($z = n\cdot$ e – charge of ion). Each chemical element is characterized by its isotopic pattern in a given mass range (see Section 6.1.1.), which means the number of isotopes at certain mass numbers of a specific element exist and the isotope abundances. For example, rubidium has two isotopes at mass numbers 85 and 87 with the isotope abundances of 72.17 % and 27.83 %. This knowledge is the basis of a qualitative identification of element. If an identification of an element is doubtful (e.g., due to possible isobaric interferences) an exact mass determination of isotopes in the mass spectrum measured at higher mass resolution is required. Therefore in the past, one of the most important tasks of mass spectrometry was the determination of isotopic abundances (the isotopic composition of elements) in nature and later the exact measurement of the atomic mass (mass of atom). The unit of atomic mass u is an abbreviation of ‘mass unit’ (sometimes amu – atomic mass unit – is used in the literature). The atomic weight of an element (A_r(E) (mean) relative atomic mass) is then the weighted average of all naturally occurring atomic masses of isotopes of this element (E).

By means of mass spectrometry, the mass of atoms and molecules, via mass-separated charged atomic or polyatomic ions, can be determined by measuring the mass-to-charge ratio (m/z), whereby the mass of an atom or a molecule is not measured in g or kg, but in a multiple of the atomic mass constant m_u (atomic mass unit). The atomic mass unit m_u is defined as one-twelfth the mass of a neutral ^{12}C atom, m_a (^{12}C), in its ground state:

$$m_u = 1\ u = m_a(^{12}C)/12 \tag{2}$$

In the older literature before 1961, the mass unit of the oxygen atom ^{16}O (MU) was proposed with:

$$1MU = m_a(^{16}O)/16 \tag{3}$$

$$\text{whereby}\quad 1\ m_u = 1\ u = 1.000317917\,MU. \tag{4}$$

The atomic mass unit (m_u) is also called the dalton (Da) – in honour of John Dalton. In response to the increase in the use of the name ‘dalton’ for the unified atomic mass unit among chemists, it was suggested by IUPAC that the unified atomic mass unit (u) be renamed the ‘dalton’ (Da). The definition of the unit would remain unchanged as one-twelfth the mass of a neutral ^{12}C atom in its ground state. The International Union of Pure and Applied Chemistry (IUPAC) proposed that both units, u and Da, should be allowed in official use.

For the calculation of the mass of an atom, molecule or ion in kg the following equation (Equation 5) for the atomic mass constant m_u can be applied:

$$m_u = 1\ u = 1\ D = 1.6605402 \cdot 10^{-27}\,kg \tag{5}$$

An advantage of the definition of mass unit is that the mass of an atom or molecule can be characterized by a full number – the mass number A, which is equal to the number of nucleons (see Equation 1). The mass of an atom or atomic mass (m_a) can be calculated approximately by the following equation (Equation 6):

$$m_a \approx A \cdot m_u \tag{6}$$

In addition, the elementary charge (e) – charge of the electron or proton – measured in Coulomb (C) is defined as:

$$\mathrm{e} = 1.60217733 \cdot 10^{-19}\mathrm{C} \tag{7}$$

In mass spectrometry, the mass-to-charge ratio (m/z) is mostly measured as a dimensionless number. Sometimes the unit known as the Thomson [Th], in honour of J. J. Thomson, is applied.

From nuclear physics it is known that the mass of a nucleus is always less than the sum of the masses of its components, the protons and neutrons. This phenomenon – called the mass defect (Δm) – seems to be in conflict with the law of conservation of mass. The mass defect $\Delta\mathrm{m}$ can be calculated by comparing the atomic weight of the nucleus m_k with the sum of the masses of the protons $\mathrm{m_p}$ and neutrons $\mathrm{m_n}$:

$$\Delta m = (Z \cdot \mathrm{m_p} + N \cdot \mathrm{m_n}) - m_\mathrm{k} \tag{8}$$

where $Z =$ number of protons and $N =$ number of neutrons.

The mass defect (mass excess) or of a nucleus is equivalent to the binding energy of the nucleons in the nucleus and corresponds to:

$$\Delta m = \Delta E/\mathrm{c}^2 \tag{9}$$

according to Einstein's relativity theory, whereby c is the speed of light in a vacuum with $\mathrm{c} = 2.99792 \times 10^8\,\mathrm{m\,s^{-1}}$. For example, for ^{4}He the mass defect Δm is 0.0304 u. Because $1\mathrm{u} = 931.494\,\mathrm{MeV\,c^{-2}}$, the bond energy of the ^{4}He nucleus is 28.3 MeV. The average bond energy of each of the four nucleons in the nucleus helium is about 7 MeV.

In contrast to isotopes of elements which contain the same number of protons, but a different number of neutrons, isobars possess the same number of nucleons (mass number A) but different numbers of protons (which means they differ in atomic numbers and therefore they are different chemical elements), e.g., ^{40}Ca and ^{40}Ar; ^{58}Fe and ^{58}Ni; ^{92}Zr and ^{92}Mo; ^{142}Ce and ^{142}Nd; ^{204}Hg and ^{204}Pb and others.

The isotopic composition of the elements (including the exact atomic mass and the abundance of the isotopes), the atomic weights of elements, definitions and abbreviations are summarized in Appendix II.

To study the isotopic pattern (isotopic abundances in dependence of m/z ratio) which is different for the chemical elements and to determine the chemical composition of any type of sample (gases, liquids or solids) mass spectrometry is the method of choice. All types of mass spectrometric systems for analysis of inorganic and organic compounds use the same basic principle. A general setup of a mass spectrometer and the principle of operation for the qualitative and quantitative analysis of inorganic or organic compounds are given in Figure 1.1 and Figure 1.2, respectively. The sample to be analyzed (gas, liquid or solid material) is inserted into the ion source. Liquids are introduced, e.g., by nebulization of the solution, and solids by evaporation e.g., by laser ablation, electrothermal evaporization or by using Knudsen effusion. The solid sample is often directly inserted into the ion source (e.g., as electrodes in spark source mass spectrometry (SSMS), as a target in laser ionization mass spectrometry (LIMS) or as cathode material in glow discharge mass spectrometry (GDMS)). In the ion source operating at high vacuum conditions, at low pressure or at atmospheric pressure, the sample material is vaporized, atomized and ionized, whereby mostly positively singly charged ions are used for analytical purposes. The positively charged ions are extracted and accelerated from their original place of generation in the ion source on the entrance slit S of the mass separation system (mass analyzer). Whereas the ion source normally lies at a positive potential, the entrance slit has a potential of zero (see Figure 1.2). After extraction of ions from the ion source to the entrance slit S of the mass spectrometer, the ions then have the potential energy eV, where V is the acceleration voltage and e is the electrical charge of a single charged ion (with $z = 1$), which is the same as the elementary charge of an electron (see Equation 7). This potential energy of the ions is transformed completely into kinetic energy ($^1\!/_2\, mv^2$, where $v =$ velocity of ions) after passing through the entrance slit S. If the initial energy of the ions received upon formation is negligibly small in comparison to the accelerating energy of the ions by extraction to the entrance slit, then the following equation is valid due to the principle of the conservation of energy:

$$\mathrm{eV} = {}^1\!/_2\, mv^2 \tag{10}$$

This fundamental equation explains that the velocity of heavier ions (v_1 of ions with mass m_1) is lower than of lighter ions (v_2 of ions with mass m_2, with $m_1 > m_2$). Equation (10) is used directly in time resolved measurements, for example in time-of-flight mass spectrometers (ToF-MS). The charged ions of the extracted and accelerated ion beam are separated by their mass-to-charge ratio, m/z, in the mass analyzer. Mass-separated ion beams are subsequently recorded by an ion detection system either as a function of time or simultaneously. Mass spectrometers are utilized for the determination of absolute masses of isotopes, atomic weights, relative abundance of isotopes and for quite different applications in survey, trace, ultratrace and surface analysis as discussed in Chapters 8 and 9.

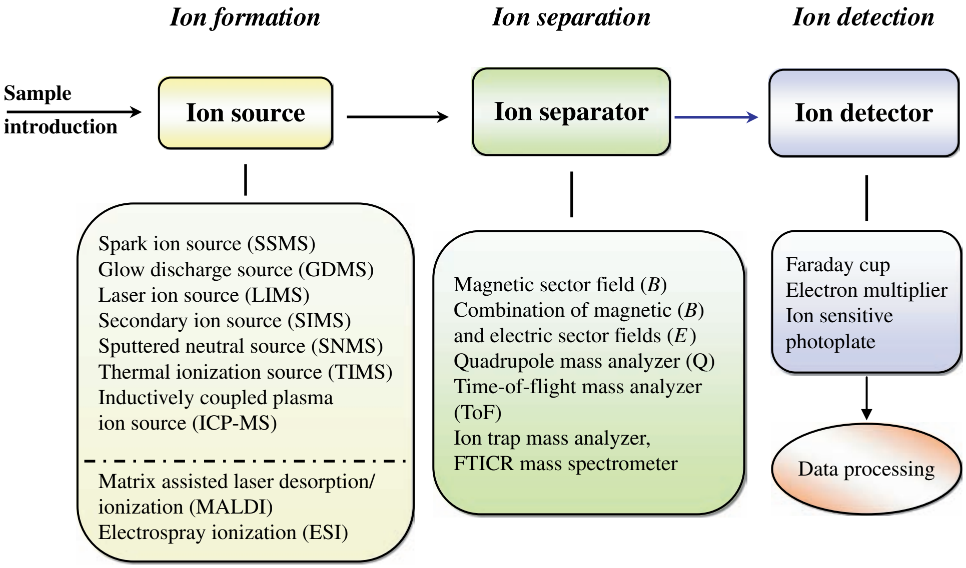

Figure 1.1 *Basic diagram of mass spectrometry: generation of ions from compounds in the sample, introduction into the ion source, separation of these ions by their mass-to-charge ratio in the mass separator and detection of ions in the ion detector.*

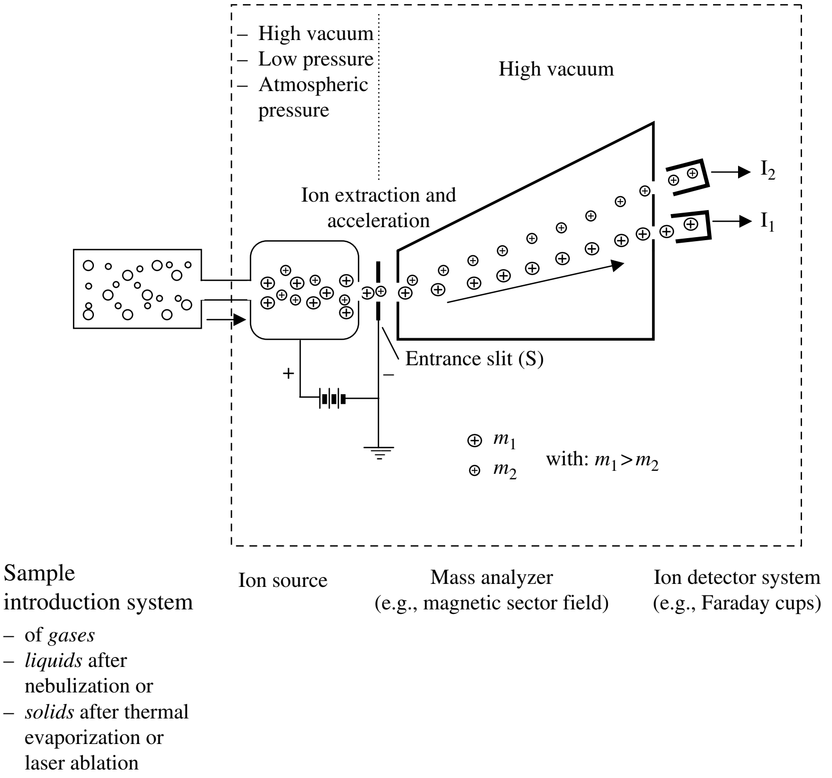

Figure 1.2 *Principle of the operation of a mass spectrometer including sample introduction system, ion source, mass separator (e.g., a magnetic sector field) and ion detector system (e.g., double ion collectors for simultaneous measurements of two separated ion beams).*

Inorganic mass spectrometric techniques, such as ICP-MS, laser ablation ICP-MS (LA-ICP-MS), glow discharge mass spectrometry (GDMS), secondary ion mass spectrometry (SIMS) and accelerator mass spectrometry (AMS), have been established in the last few decades as the most important and sensitive analytical techniques for elemental, surface and isotope analysis at the trace and ultratrace concentration level and for the analysis of species. Furthermore, special mass spectrometric techniques – secondary ion mass spectrometry (SIMS) and sputtered neutral mass spectrometry (SNMS) – have achieved significance as reliable surface analytical techniques with a spatial resolution in the μm and sub-μm range and depth resolution in the nm range, respectively. The capabilities and applications of different inorganic mass spectrometric methods have to be judged with respect to their advantages and drawbacks, also in comparison to non-mass-spectrometric analytical techniques.

In addition, one of the main features of mass spectrometry is, and this is the major advantage in comparison to other atomic and molecular non-mass spectrometric techniques, that it offers the possibility of determining isotope ratios and abundances of isotopes with high precision and accuracy in all types of samples (in solid, liquid and gaseous materials as well). Isotope ratio measurements have applied increasingly for stable isotopes in nature, especially for investigating fine isotope variation in nature or age dating, for process analysis and process control, for determining isotope ratios of radiogenic elements in the nuclear industry, quality assurance of fuel material, for reprocessing plants, nuclear material accounting and radioactive waste control, and for tracer experiments using stable isotopes or long-lived radionuclides in biological or medical studies. On the basis of known isotopic compositions, major, minor, trace and ultratrace element concentrations can be determined in any materials.

Accordingly, developments in all fields of mass spectrometry have been prompted in the past by requests from industry, research and routine laboratories for sensitive and accurate multi-element analytical techniques at the trace and ultratrace level. It is interesting to note that the most important meetings for the international community of plasma and mass spectroscopists – the annual Winter Conference on Plasma Spectrometry alternately in the USA or Europe and two in Asia (2005, 2006) and the Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, FACSS – have been dominated more and more by recent mass spectrometric developments, especially in inductively coupled plasma mass spectrometry (ICP-MS) involving hyphenated techniques resulting in powerful speciation analysis, and nowadays in combination with organic mass spectrometry in protein research, especially for analysis of metal-, selenium- and phosphorus-containing proteins. The International Mass Spectrometry Conference (IMSC, 2006 in Prague) and the annual American Society of Mass Spectrometry Conference (ASMS) have been focused more on organic and especially by bioorganic mass spectrometric developments and application. New developments and applications of surface analytical techniques have been presented at International and European SIMS Conferences and in scientific journals such as *Thin Solid Films, Applied Surface Science, Surface Coating Technology, Chemical Geology* and others. Simultaneously with the increasing installation of ICP-MS instruments worldwide, a rapid increase has also been observed in the number of analytical publications in the *Journal of Analytical Atomic Spectrometry, Analytical Chemistry, International Journal of Mass Spectrometry, Analytical and Bioanalytical Chemistry* (formerly *Fresenius' Journal of Analytical Chemistry), Atomic Spectrometry, Spectrochimica Acta B, Analyst* and others.

Trends in mass spectrometry focus on the improvement of instrumentation, of several techniques in order to minimize sample volume, to improve sensitivity and to reduce detection limits. This is combined with increasing the speed of several analyses, with automation of analytical procedures and subsequently reducing the price of analysis. A minimizing of sample volumes means a reduction of waste volume with the aim of developing 'green chemistry'. Furthermore, new analytical techniques involve a development of quantification procedures to improve the accuracy and precision of analytical data. Special attention in future will be given to the development of hyphenated mass spectrometric techniques for speciation analysis and of surface analytical techniques with improved lateral resolution in the nm scale range.

1

History of Mass Spectrometric Techniques

In its history, mass spectrometry has passed through fascinating scientific epochs of development and supplied important contributions to the world view in quite different fields of science (especially in the life sciences, environmental science and technology, material and nuclear sciences, geosciences, cosmochemistry,[1] planetary and forensic sciences) and in basic studies in chemistry and physics.

Mass spectrometry is more than 100 years old and has yielded basic results and profound insights for the development of atomic physics. The rapid development of nuclear physics, in particular, would be unthinkable without the application of mass spectrometric methods. Mass spectrometry has contributed to conclusive evidence for the hypothesis of the atomic structure of matter. So far mass spectrometry has supplied specific results on the structure of the nucleus of atoms. Nobel prizes have been awarded to a number of scientists (Thomson, Wien, Aston, Paul, Fenn and Tanaka) associated with the birth and development of mass spectrometry, or in which mass spectrometry has aided an important discovery (e.g., for the discovery of fullerenes by Curl, Kroto and Smalley).

Relevant preliminary work for the development of mass spectrography started with Goldstein's discovery of anode rays, which are positive charged gas-phase ions, in gas discharge in the mid-1980s. The experimental arrangement of Goldstein's glow discharge tube as the simplest possible ion source is shown in Figure 1.3 and was firstly published in the '*Sitzungsbericht der Königlich-Preußischen Akademie der Wissenschaften*' in 1886.[2] Goldstein's method for generating positively charged ions in a gas discharge was used in the early mass analysis measurements of Wien,[3] Thomson[4] and Aston.[5] In 1898 Wien analyzed the anode rays by magnetic deflection and found that these rays carried a positive charge. The schematic of a Wien velocity filter with *EB* configuration (*E* – electrical sector field and *B* – magnetic sector field) is shown in Figure 1.4. In this experimental arrangement, the deflection of positively charged ions in a magnetic field is compensating by a superimposed deflection in an electrical field. For ions which are transmitted through a Wien

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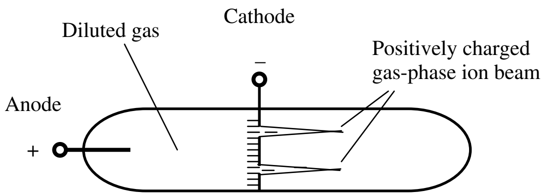

Figure 1.3 *Goldstein's glow discharge tube (1886) for generation of positively charged ions. (C. Brunnée, Int. J. Mass. Spectrom. Ion Proc. 76, 125 (1987). Reproduced by permission of Elsevier.)*

velocity filter it is valid that the electrical force (e E) that acts on an ion is equal the Lorentz force (e v B):

$$\mathrm{e}\,E = \mathrm{e}\,v\,B \tag{1.1}$$

The velocity of the ion (v) can be described then as the ratio of electrical field force (E) and magnetic field force (B):

$$v = E/B \tag{1.2}$$

$$\text{with} \quad v = \sqrt{2\mathrm{e}V/m} \tag{1.3}$$

The Wien velocity filter possesses a high sensitivity and allows analysis over a mass range (using a high accelerating voltage V), but with increasing mass the mass resolution decreases.[3] For his discovery Wien was honoured with the Nobel Prize in 1911.

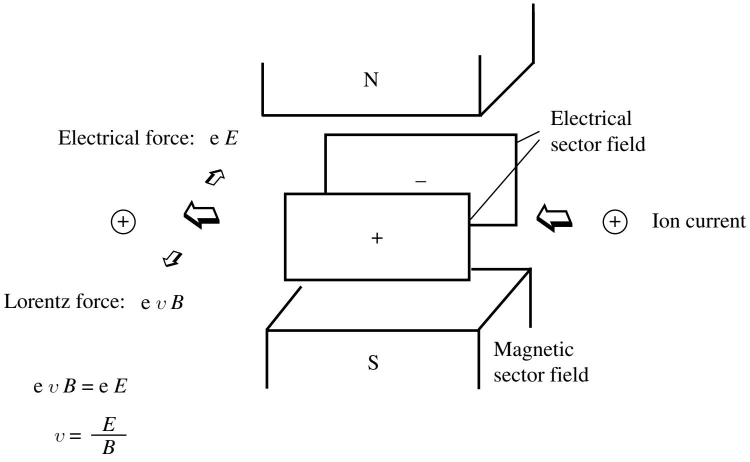

Figure 1.4 *Schematic of a Wien velocity filter with EB configuration: combination of electric (E) and magnetic (B) field (Wien,1898). (C. Brunnée, Int. J. Mass. Spectrom. Ion Proc. 76, 125 (1987). Reproduced by permission of Elsevier.)*