Chapter 1

Introduction

1.1 Considering the Role of X-ray Spectrometry in Chemical Analysis and Outlining the Volume

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1.1.1 RATIONALE

Basic X-ray spectrometry (XRS) is, of course, not a new technique. The milestone developments that shaped the field all took place several decades ago. Soon after the discovery of X-rays in 1895 by Wilhelm Conrad Röntgen, the possibility of wavelength-dispersive XRS (WDXRS) was demonstrated and Coolidge introduced the high-vacuum X-ray tube in 1913. There was quite a time gap then until Friedmann and Birs built the first modern commercial X-ray spectrometer in 1948. The fundamental Sherman equation, correlating the fluorescent X-ray intensity quantitatively with the chemical composition of a sample, dates back to 1953. The fundamental parameter (FP) approach, in its earliest version, was independently developed by Criss and Birks and Shiraiwa and Fujino, in the 1960s. Also various practical and popular influence coefficient algorithms, like those by Lachanche–Traill, de Jongh, Claisse–Quintin, Rasberry–Heinrich, Rousseau and Lucas–Tooth–Pine all date back to 1960–1970. The first electron microprobe analyser (EMPA) was successfully developed in 1951 by Castaing, who also outlined the fundamental aspects of qualitative electron microprobe analysis. The first semiconductor Si(Li) detectors, which heralded the birth of energy-dispersive XRS (EDXRS), were developed, mainly at the Lawrence Berkeley Lab, around 1965. Just before 1970, accelerator-based charged-particle induced XRS or proton-induced X-ray emission (PIXE) analysis was elaborated; much of the credit went to the University of Lund in Sweden. A description of the setup for total-reflection X-ray fluorescence (TXRF) was first published by Yoneda and Horiuchi and the method was further pursued by Wobrauschek and Aiginger, both in the early 1970s. The advantages of polarised X-ray beams for trace analysis were pointed out in 1963 by Champion and Whittam and Ryon put this further into practice in 1977. There have been demonstrations of the potential for micro-X-ray fluorescence (XRF) since 1928 (by Glockner and Schreiber) and Chesley began with practical applications of glass capillaries in 1947. Synchrotron-radiation (SR) XRS was introduced in the late 1970s and Sparks developed the first micro version at the Stanford Synchrotron Radiation Laboratory in 1980.

So around 1990, there was a feeling that radically new and stunning developments were
lacking in XRS and scientists began to have some ambivalent opinions regarding the future role of XRS in analytical chemistry. One could wonder whether, in spite of remarkably steady progress, both instrumental and methodological, XRS had reached a state of saturation and consolidation, typical for a mature and routinely used analysis technique.

In the meantime, XRF had indeed developed into a well-established and mature multi-element technique. There are several well-known key reasons for this success: XRF is a universal technique for metal, powder and liquid samples; it is non-destructive; it is reliable; it can yield qualitative and quantitative results; it usually involves easy sample preparation and handling; it has a high dynamic range, from the ppm level to 100% and it can, in some cases, cover most of the elements from fluorine to uranium. Accuracies of 1% and better are possible for most atomic numbers. Excellent data treatment software is available allowing the rapid application of quantitative and semi-quantitative procedures. In the previous decades, somewhat new forms of XRS, with e.g. better sensitivity and/or spectral resolution and/or spatial resolution and/or portable character, had been developed. However, alternative and competitive more sensitive analytical techniques for trace analysis had, of course, also been improved; we have seen the rise and subsequent fall of atomic absorption spectrometry and the success of inductively coupled plasma atomic emission and mass spectrometry (ICP-AES and ICP-MS) in the last two decades.

Since 1990, however, there has been dramatic progress in several sub-fields of XRS, and in many aspects: X-ray sources, optics, detectors and configurations, and in computerisation and applications as well. The aim of the following chapters in this book is precisely to treat the latest and often spectacular developments in each of these areas. In principle, all references will pertain to the last 5–6 years. Many of the chapters will have a high relevance for the future role of XRS in analytical chemistry, but certainly also for many other fields of science where X-rays are of great importance. The following sections in this chapter will give a flavour of the trends in the position of different sub-fields of XRS based e.g. on the recent literature and will present the outline of this volume.

### 1.1.2 THE ROLE AND POSITION OF XRS IN ANALYTICAL CHEMISTRY

An attempt has been made to assess the recent trends in the role and position of XRS based on a literature survey (see also Injuk and Van Grieken, 2003) and partially on personal experience and views. For the literature assessment, which covered the period from January 1990 till the end of December 2000, a computer literature search on XRS was done in *Chemical Abstracts*, in order to exclude (partially) the large number of XRS publications on astronomy, etc.; still, it revealed an enormous number of publications. Figure 1.1.1 shows that the volume of the annual literature on XRS, cited in *Chemical Abstracts*, including all articles having ‘X-ray spectrometry/spectroscopy’ in their title, is still growing enormously and exponentially. During the last decade, the number of publications on XRS in general has nearly doubled; in 2000, some 5000 articles were published, versus 120 annually some 30 years ago. As seen in Figure 1.1.2, XRS in general seems more alive than ever nowadays.

However, the growth of the literature on specifically XRF is much less pronounced: from about 500 articles per year in 1990 to about 700 in 2000, still a growth of 40% in the last decade. While in 1990 it looked like XRF had reached a state of saturation and consolidation, newer developments in the 1990s, e.g. the often-spectacular ones described in the other chapters of this volume, have somehow countered such fears. It is a fact that WDXRF remains the method of choice for direct accurate multi-element analysis in the worldwide mineral and metallurgy industry. For liquid samples, however, the competition of ICP-AES and ICP-MS remains formidable. It is striking that, while there are still many more WDXRF units in operation around the world than EDXRF instruments, the number of publications dealing with WDXRF is about five times lower. This clearly reflects the predominant use of the more expensive WDXRF
in routine industrial analysis, where publishing is not common, while EDXRF is mostly present in academic and research institutions; there are many applications in environment-related fields where ultimate accuracies are not so mandatory.

Also the number of publications on radioisotope XRF has been increasing from 40 in 1990 to 100 in 1998, reflecting the frequent use of the technique in many field and on-line applications. In Australia alone, more than 2000 portable XRF are employed in the mining and mineral industry. It is expected that the radioisotope-based on-line installations will gradually be replaced by systems based on small X-ray tubes.

The annual number of articles dealing with various aspects of the PIXE technique (but excluding micro-PIXE) is in the range of 30 to 70 with very prominent peaks every 3 years. These
are obviously related to the publication of the proceedings of the tri-annual PIXE Conferences (Figure 1.1.3), with many short articles. It is clear, and not only from the literature, that, of all X-ray emission techniques considered, PIXE is thriving the least; there is no clear growth in the literature, although PIXE might still be the method of choice for the trace analysis of large numbers of relatively small samples, like e.g. for particulate air pollution monitoring using impactor deposits of aerosols. The number of PIXE installations in the world is probably decreasing, and the future of PIXE seems to be exclusively in its micro version; some 30 institutes are active in this field at the moment. The literature on micro-PIXE is still growing; a search on Web of Science showed that the annual number of articles on micro-PIXE was around 10 at the beginning of the previous decade and around 35 in the last few years.

Since the early 1970s, SR-XRS has been experiencing remarkable growth, nowadays approaching almost 350 articles per year, with a doubling seen over the last decade. Investment in SR facilities continues to be strong and with the increasing availability of SR X-ray beam lines, new research fields and perspectives are open today. Most of the presently operational SR sources belong to the so-called second-generation facilities. A clear distinction is made from the first generation, in which the SR was produced as a parasitic phenomenon in high-energy collision experiments with elementary particles. Of special interest for the future are new third-generation storage rings, which are specifically designed to obtain unique intensity and brilliance. SR has a major impact on microprobe-type methods with a high spatial resolution, like micro-XRF, and on X-ray absorption spectrometry (XAS) as well as on TXRF. For highly specific applications, SR-XRS will continue to grow. The costs of SR-XRS are usually not calculated, since in most countries, SR facilities are free of charge for those who have passed some screening procedure. Of course, such applications cannot be considered as routine.

There are nowadays some 100 publications annually on TXRF, and this number has more or less doubled since 1990. However, it may seem that TXRF has stabilized as an analytical method for ultra-trace determination from solutions and dissolved solids due to the fierce competition from ICP-MS, in particular. There are now only a few companies offering TXRF units. But mostly for surface analysis directly on a flat solid sample, TXRF is still unique. SR-TXRF might be one of the methods of choice in future wafer surface analysis (in addition to e.g. secondary ion mass spectrometry). In addition, by scanning around the total-reflection angle, TXRF allows measurements of the density, roughness and layer thickness and depth profiling, which are, of course, of much interest in material sciences. New possibilities for improving the performance of TXRF are in using polarised primary radiation. SR has almost ideal features for employment in combination with

![Figure 1.1.3](image-url)
TXRF. It is several orders (8–12) of magnitude higher in brightness compared to X-ray tubes, has a natural collimation in the vertical plane and is linearly polarised in the plane of the orbit of the high energy (GeV) electron or positrons. The spectral distribution is continuous, so by proper monochromatisation, the performance of selective excitation at best conditions is possible. SR offers a significant reduction in TXRF detection limits and a remarkable improvement has been achieved over the past 20 years from nanogram level in 1975 to attogram level in 1998.

Until recently, evolution of XRF into the microanalytical field was hampered because of the difficulties involved in focusing a divergent X-ray beam from an X-ray tube into a spot of small dimensions. However, the development of SR sources and the recent advances in X-ray focusing have changed the situation. Contemporary micro-XRF applications started only some 10 years ago on a significant scale, and it appears today to be one of the best microprobe methods for inorganic analysis of various materials: it operates at ambient pressure and, in contrast to PIXE and EMPA, no charging occurs. In many instances, no sample preparation is necessary. The field of micro-XRF is currently subject to a significant evolution in instrumentation: lead-glass capillaries and polycapillary X-ray lenses, air-cooled micro-focus X-ray tubes, compact ED detector systems with a good resolution even at a high-count rate and no longer requiring liquid-nitrogen cooling. Commercial laboratory instrumentation using capillary optics combined with rapid scanning and compositional mapping capability is expected to grow, and various systems are commercially available. During the 1980s, SR facilities around the world began to implement X-ray microbeam capabilities on their beam lines for localised elemental analysis. Recent trends in SR micro-XRF are towards optimisation of optics and smaller beam sizes down to the submicrometer size.

With respect to the general applications of XRS, it appears that environmental, geological, biological and archaeological applications make up a stunning 70% contribution to the literature; undoubtedly this is far above their relative contributions in actual number of analysis, since XRF is certainly still a working horse in many types of industries, for all kinds of routine analyses, but the latter applications are published very seldom. The number of articles dealing with environmental applications of XRS, in the past decade, shows a steady growth. Interestingly, the relative contributions for the different topics covered in the environmental applications, like soils and geological material (23%), biological materials (19%), water (19%), air (17%) and waste material (8%) have not changed considerably during the last decade.

Table 1.1.1 shows the relative share of laboratories in different countries to the literature on XRS generated in 1998 (according to Analytical Abstracts) and the language in which the publications were written. It appears that European countries produce almost one half of the total number of publications, while, of the non-European countries, China and Russia are leading. The low contribution of the USA is striking. There might be several reasons for this. Apparently, XRS is considered more as a routine technique by the US industry and there are almost no US academic centers working in this field. It is also true that in 1998, no volume of Advances in X-ray Analysis appeared and this covers the proceedings of the popular Denver X-ray

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<th>Country</th>
<th>Relative contribution (%)</th>
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<tr>
<td>Russia</td>
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<td>Japan</td>
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<td>USA</td>
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Analysis Conference. Finally, the most advanced research (as described in the following chapters in this volume) may still be published in physics journals rather than in journals covered by Analytical Abstracts. It also appeared from our literature search that about one fourth of the XRS literature is written in less accessible languages like Russian, Chinese and Japanese.

In view of the enormous advances that are being made in XRS and that, hopefully, are covered well in the following chapters of this book, one can expect that the applications of XRS will dramatically be changed over the next few years, and that, in the literature, the distribution over fundamental aspects (probably not fully reflected yet in the literature covered by Chemical Abstracts and Analytical Abstracts discussed above) will be radically different as well.

1.1.3 VOLUME OUTLINE

All of the chapters of this volume have been written by acknowledged research and application leaders, the best that the editors could find in each of the sub-fields. A relatively large fraction of them are Japanese scientists, and this may be a bonus for readers elsewhere in the world, since only about half of the advanced XRS research in Japan is published in English and hence it is not always sufficiently widely known, e.g. in the West.

All the chapters or sets of subchapters cover topics in which remarkable progress has been made during the last decade and which offer good perspective for drastically changing the power of XRS in the near future.

Chapter 2 deals with X-ray sources, which have become more powerful and diverse in the last few years. Significant improvements have been made to the design and performances of conventional X-ray tubes, and in their miniaturisation (which is treated in a later chapter), but most impressive has been the progress in micro-X-ray sources, the development of new synchrotron sources and the first steps towards X-ray laser and laser-induced plasma X-ray sources applicable to XRS. Subchapter 2.1 (by M. Taylor, R. Bytheway and B. K. Tanner of Bede plc, Durham, UK) describes how electromagnetic rather than conventional electrostatic focusing, for shaping and steering the electron beam in the X-ray tube, allows the X-ray source dimensions to be controlled much better than in the past, to achieve a higher brilliance without target damage, to tailor the X-ray spot dimensions for optimising the input coupling with subsequent grazing-incidence X-ray optical elements, like ellipsoidal mirrors and polycapillaries (treated in a later chapter), and hence to deliver high brilliance beams of small dimension to the sample. These high-brightness micro-focus sources have been used mostly in X-ray diffraction (XRD) so far, but they are likely to have a major impact on XRS in the near future as well. Subchapter 2.2 on new synchrotron radiation sources was written by M. Watanabe (Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan) and G. Isoyama (Institute of Scientific and Industrial Research, Osaka University, Japan). In this subchapter, new synchrotron radiation sources are introduced and the characteristics of synchrotron radiation are summarised. New aspects and typical properties of the synchrotron radiation flux at the sample position are described for users of third-generation sources and candidates for fourth-generation sources are discussed. In Subchapter 2.3, C. Spielman (Physikalisches Institut EP1, University of Würzburg, Germany) treats a novel generation of laser-driven X-ray sources, which could produce femtosecond pulses of soft to hard X-rays, synchronisable to other events, and very high intensities, from compact laboratory X-ray sources. This section describes recent progress in the development of laser sources relevant for X-ray generation and reviews the generation of laser-produced incoherent radiation, the development of X-ray lasers and high-harmonic generation. Applications of coherent laboratory X-ray sources are still in their infancy, but these might be intriguing in the future, in XRS, X-ray microscopy, X-ray photoelectron spectroscopy and maybe X-ray interferometry, all of which have had to rely on large-scale synchrotron facilities thus far, and might open the way to attosecond science.
The third chapter is all about X-ray optics, another field that has seen an explosive growth in the last decade, in various ways, resulting in new commercial instruments and new application lines. In Subchapter 3.1, M. Yanagihara (Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan) and K. Yamashita (Department of Physics, Nagoya University, Japan) discuss advances in multilayer production technology, due to the progress in thin-film technology and polishing of super-smooth substrates to the sub-nanometer level, and in their performance and applications. For soft X-rays, the latter include focusing, microscopy and polarimetry; for hard X-rays, obtaining microbeams for microscopy, X-ray telescopes and multilayer-coated gratings are discussed. In Subchapter 3.2, Y. Hosokawa (X-ray Precision, Inc., Kyoto, Japan) presents the state-of-the-art for single capillaries, which make use of multiple external total reflections. He shows how a very bright and narrow X-ray microbeam can be realised using single capillaries (or X-ray guide tubes), and how this leads to a tabletop X-ray analytical microscope. Several applications are presented. In Subchapter 3.3, N. Gao (X-ray Optical Systems, Albany, NY, USA) and K. Janssens (University of Antwerp, Belgium) give a detailed treatment of the fundamentals of multi-fiber polycapillaries and the recent fused and heat-shaped monolithic versions. In the last decade, polycapillary optics have become widespread and successfully used as crucial components in commercial X-ray microanalysis and low-power compact instruments. Novel analytical applications are situated in elemental microanalysis in laboratory scale, portable and synchrotron systems, micro-X-ray absorption near-edge spectroscopy (XANES), EMPA, etc. Future developments in performance and spot size are discussed. Finally, the new compound refractive lenses, first fabricated in 1996, are presented in Subchapter 3.4 by A. Simionovici (European Synchrotron Research Facility, Grenoble, France) and C. Schroer and B. Lengeler (Aachen University of Technology, Germany). Their theory, design and properties are considered, as well as their use for imaging and microbeam production. Some focus is on parabolic refractive X-ray lenses that can be used in e.g. a new hard X-ray microscope that allows sub-micrometer resolution and for e.g. combined fluorescence spectroscopy and tomography. Applications in the realms of biology, XRF computed micro-tomography, geochemistry and environmental research are given.

The most dramatic and spectacular progress has certainly been made recently in the field of X-ray detector technology, and all this is covered in Chapter 4. In Subchapter 4.1, L. Strüder, G. Lutz, P. Lechner, H. Soltau and P. Holl (Max-Planck-Institute for Physics and Extraterrestrial Physics, pnSensor and/or the Semiconductor Lab of the Max Planck Institute, Munich, Germany) treat advances in silicon detectors. After an introduction to the basic operation principles of semiconductors and the electronics used, some important new detectors are discussed in detail and important applications in XRS and imaging are reviewed. The detectors include Silicon Drift Detectors for X-ray detection, Controlled Drift Detectors (CDD), fully depleted backside illuminated pn-CCD and Active Pixel Sensors (APS) for XRS. All these quite sophisticated detectors have left their initial fields of applications in high-energy physics, astrophysics and SR research. They are now a mature technology and open many new industrial applications. These detectors exhibit now a high quantum efficiency, excellent energy resolution, high radiation tolerance, good position resolution, high speed, homogeneous response of the full bandwidth of radiation and high background rejection efficiency. In Subchapter 4.2, C. A. N. Conde (Department of Physics, University of Coimbra, Portugal) treats the role of new gas proportional scintillation counters (GPSC) for XRS, after considering the physics of the absorption of X-rays in gases, the transport of electrons and the production of electroluminescence in gases, and the basic concepts of different types of GPSC. Their energy resolution is only 8\% for 5.9 keV X-rays, but they can be built with very large windows and be useful for very soft X-rays like the K-lines of C and O. Different types of cryogenic detectors, operating near the liquid helium temperature (implying sophisticated cooling systems) and offering unseen energy
resolutions, are truly a major development of recent years. However, their commercial availability and price range is still somewhat unclear at the moment. Both superconducting tunneling junctions (STJ) and microcalorimeters are treated in detail in this volume. In Subchapter 4.3, M. Kurakado (Department of Electronics and Applied Physics, Osaka Electro-Communication University, Japan) explains the unique working principles of STJ, which usually consist of two superconductor layers and a nanometer-thick insulator layer, which is a tunnel barrier between the superconductor layers that can be passed by excited electrons or holes, i.e. quasiparticles, to give rise to a signal. Single-junction detectors and two other types of STJ detectors are discussed. Fantastic energy resolutions around 10 eV are possible. New applications are emerging, including one- and two-dimensional imaging. Other equally promising cryogenic detectors are the cryogenic microcalorimeters, treated in Subchapter 4.4 by M. Galeazzi (Department of Physics, University of Miami, Coral Gables, FL, USA) and E. Figueroa-Feliciano (NASA/Goddard Space Flight Center, Greenbelt, MD, USA). The idea of detecting the increase in temperature produced by incident photons instead of the ionisation of charged pairs, like in semiconductor detectors, was put forward almost 20 years ago, and the operating principle is rather simple, but the practical construction is quite challenging. Only in recent years has the practical construction of adequate cryogenic microcalorimeters been realised. The required characteristics, parameters and non-ideal behavior of different components and types, including large arrays, detector multiplexing and position-sensitive imaging detectors, are discussed in detail. Several expected future developments are outlined. In the last section of this chapter on detectors, W. Dabrowski and P. Gryboś (Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, Krakow, Poland) treat position-sensitive semiconductor strip detectors, for which the manufacturing technologies and readout electronics have matured recently. Silicon strip detectors, of the same type as used for detection of relativistic charged particles, can be applied for the detection of low-energy X-rays, up to 20 keV. Regardless of some drawbacks due to limited efficiency, silicon strip detectors are most widely used for low-energy X-rays. Single-sided, double-sided and edge-on silicon strip detectors and the associated electronics are treated in great detail.

There are many special configurations and instrumental approaches in XRS, which have been around for a while or have recently been developed. Eight of these are reviewed in Chapter 5. In Subchapter 5.1, K. Sakurai (National Institute for Materials Science, Tsukuba, Japan) deals with TXRF or grazing-incidence XRF (GI-XRF). Although TXRF may have been fading away a bit recently for trace element analysis of liquid or dissolved samples, there have still been advances in combination with wavelength-dispersive spectrometers and for low atomic number element determinations. But mostly, there have recently been interesting developments in surface and interface analysis of layered materials by angular and/or energy-resolved XRF measurements, and in their combination with X-ray reflectometry. Micro-XRF imaging without scans is a recent innovation in GI-XRF as well. Future developments include e.g. combining GI-XRF with X-ray free-electron laser sources. An approach that has not been used widely so far is grazing-exit XRS (GE-XRS), related in some ways to GI-XRF. GE-XRF is the subject of Subchapter 5.2, by K. Tsuji (Osaka City University, Japan). Since the X-ray emission from the sample is measured in GE-XRS, different types of excitation probes can be used, not only X-rays but also electrons and charged particles. In addition, the probes can be used to irradiate the sample at right angles. This subchapter describes the principles, methodological characteristics, GE-XRS instrumentation, and recent applications of GE-XRF, as well as GE-EPMA and GE-PIXE. At the end of this subchapter, the future of GE-XRS is discussed, which implies the use of more suitable detectors and synchrotron radiation excitation. One interesting aspect of XRF is the enormously increased recent (commercial) interest in portable EDXRF systems. This topic is treated in the next subchapter by R. Cesareo and A. Brunetti (Department of Mathematics and
Physics, University of Sassari, Italy), A. Castel-lano (Department of Materials Science, University of Lecce, Italy) and M.A. Rosales Medina (University ‘Las Americas’, Puebla, Mexico). Only in the last few years, has technological progress produced miniature and dedicated X-ray tubes, thermoelectrically cooled X-ray detectors of small size and weight, small size multichannel analysers and dedicated software, allowing the construction of completely portable small size EDXRF systems that have similar capabilities as the more elabora
tory systems. Portable equipment may be necessary when objects to be analysed cannot be transported (typically works of art) or when an area should be directly analysed (soil analysis, lead inspection testing, etc.) or when the mapping of the object would require too many samples. The advantages and limitations of different set-ups, including optics, are discussed. A focused subchapter on the important new technology of microscopic XRF using SR radiation has been produced by F. Adams, L. Vincze and B. Vekemans (Department of Chemistry, University of Antwerp, Belgium). It describes the actual status with respect to lateral resolution and achievable detection limits, for high-energy, third-generation storage rings (particularly the European Synchrotron Radiation Facility, Grenoble, France), previous generation sources and other sources of recent construction. Related methods of analysis based on absorption edge phenomena such as X-ray absorption spectroscopy (XAS), XANES, X-ray micro-computed tomography (MXCT) and XRD are briefly discussed as well. Particular attention is paid to the accuracy of the XRF analyses. Subchapter 5.5 by I. Nakai (Department of Applied Chemistry, Science University of Tokyo, Japan) deals with high-energy XRF. It considers SR sources and laboratory equipment, in particular a commercial instrument for high-energy XRF that has only recently become available. The characteristics of the technique include improved detection limits, chiefly for high atomic number elements. This makes it particularly suitable for the determination of e.g. rare earths via their X-lines. Other interesting application examples pertain to environmental, archaeological, geochemical and forensic research. Low-energy EMPA and scanning electron microscopy (SEM) are the topics of S. Kuypers (Flemish Institute for Technological Research, Mol, Belgium). The fundamental and practical possibilities and limitations of using soft X-rays, as performed in the two separate instruments, are discussed. The potential of the two techniques is illustrated with recent examples related to the development of ultra-light-element based coatings for sliding wear applications, membranes for ultrafiltration and packaging materials for meat. In Subchapter 5.7, E. Van Cappellen (FEI Company, Hillsboro, OR, USA) treats ED X-ray microanalysis in transmission electron microscopy (TEM), for both the scanning and conventional mode. The section describes how EDXRS in the (S)TEM can be made quantitative, accurate and precise, and is nowadays an extremely powerful technique in materials science and has not vanished in favor of electron energy loss spectrometry (EELS) as predicted 20 years ago. Several examples are given of quantitative chemical mapping, qualitative analysis of ionic compounds and other real-world applications. Finally, J. Kawai (Department of Materials Science and Engineering, Kyoto University, Japan) discusses in detail the advances in XAS or X-ray absorption fine structure spectroscopy (XAFS), which include XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure). X-ray absorption techniques are now used in commercially available film thickness process monitors for plating, printed circuit and magnetic disk processes, in various kinds of industries. But they are used, both in laboratories and synchrotron facilities, for basic science as well. The X-ray absorption techniques, described extensively in this subchapter, differ in probe type (electrons and X-rays, sometimes polarised or totally reflected), detected signals (transmitted X-rays, XRF, electrons, electric currents, and many others) and application fields (high temperature, high pressure, low temperature, in situ chemical reaction, strong magnetic field, applying an electric potential, short measurement time, and plasma states). One shortcoming of XAS techniques, that absorption spectra of all the elements were not measurable using one beamline,
has been overcome in many synchrotron facilities nowadays.

Chapter 6 reviews some advances in computerisation concerning XRS. The first subchapter, written by L. Vincze, K. Janssens, B. Vekemans and F. Adams (Department of Chemistry, University of Antwerp, Belgium) deals with modern Monte Carlo (MC) simulation as an aid for EDXRF. The use of MC simulation models is becoming more and more viable due to the rapid increase of inexpensive computing power and the availability of accurate atomic data for photon-matter interactions. An MC simulation of the complete response of an EDXRF spectrometer is interesting from various points of view. A significant advantage of the MC simulation based quantification scheme compared to other methods, such as FP algorithms, is that the simulated spectrum can be compared directly to the experimental data in its entirety, taking into account not only the fluorescence line intensities, but also the scattered background of the XRF spectra. This is linked with the fact that MC simulations are not limited to first- or second-order approximations and to ideal geometries. Moreover, by considering the three most important interaction types in the 1–100 keV energy range (photoelectric effect followed by fluorescence emission, Compton and Rayleigh scattering), such models can be used in a general fashion to predict the achievable analytical characteristics of e.g. future (SR)XRF spectrometers and to aid the optimisation/calibration of existing instruments. The code illustrated in this subchapter has experimentally been verified by comparisons of simulated and experimental spectral distributions of various samples. With respect to the simulation of heterogeneous samples, an example is given for the modeling of XRF tomography experiments. The simulation of such lengthy XRF imaging experiments is important for performing feasibility studies and optimisation before the actual measurement is performed. Subchapter 6.2 by P. Lemberghe (Department of Chemistry, University of Antwerp, Belgium) describes progress in spectrum evaluation for EDXRF, where it remains a crucial step, as important as sample preparation and quantification. Because of the increased count rate and hence better precision due to new detectors, more details became apparent in the spectra; fortunately, the availability of inexpensive and powerful PCs now enables the implementation of mature spectrum evaluation packages. In this subchapter, the discussed mathematical techniques go from simple net peak area determinations, to the more robust least-squares fitting using reference spectra and to least-squares fitting using analytical functions. The use of linear, exponential or orthogonal polynomials for the continuum fitting, and of a modified Gaussian and Voigtian for the peak fitting is discussed. Most attention is paid to partial least-squares regression, and some illustrative analytical examples are presented.

The final chapter, Chapter 7, deals with five growing application fields of XRS. J. Börjesson (Lund University, Malmö and the Department of Diagnostic Radiology, County Hospital, Halmstad, Sweden) and S. Mattsson (Department of Diagnostic Radiology, County Hospital, Halmstad Sweden) focus on applications in the medical sciences since 1995, i.e. on recent advances in in vivo XRF methods and their applications, and on examples of in vitro use of the technique. The latter deals mostly with the determination of heavy metals in tissues, in well-established ways. But there have been significant developments lately in in vivo analysis with respect to sources, geometry, use of polarised exciting radiation, MC simulations and calibration, and the analytical characteristics have been improved. Examples of novel in vivo determinations of Pb, Cd, Hg, Fe, I, Pt, Au and U are discussed. The next subchapter deals with novel applications for semiconductors, thin films and surfaces, and is authored by Y. Mori (Wacker-NSCE Corp., Hikari, Japan). Progress in the industrial application of TXRF in this field is first discussed. The use of TXRF for semiconductor analysis came into popular use in the 1990s; today, more than 300 TXRF spectrometers are installed in this industry worldwide, meaning that almost all leading-edge semiconductor factories have introduced TXRF. Since the main purpose of TXRF is trace contamination analysis, improvements in the elemental range (including light elements), detection ability (e.g. by preconcentration) and standardisation
(versus other techniques) are discussed. In addition, XRF and X-ray reflectivity analysers for the characterisation of thin films made from new materials are introduced. A. Zucchiatti (Istituto Nazionale di Fisica Nucleare, Genova, Italy) wrote the next subchapter on the important application of XRS in archaeometry, covering instrumentation from portable units through PIXE and synchrotrons. Applications of the latter techniques include e.g. the study of Renaissance glazed terracotta sculptures, flint tools and Egyptian cosmetics. Also the XRF and XANES micro-mapping of corroded glasses is described. Radiation damage is a constant major concern in this field. The much larger availability of facilities and several technological advances have made archaeometry a very dynamic field for XRS today and an even greater research opportunity for tomorrow. T. Ninomiya (Forensic Science Laboratory, Hyogo Prefectural Police Headquarters, Kobe, Japan) illustrates some recent forensic applications of TXRF and SR-XRF. Trace element analysis by TXRF is used to fingerprint poisoned food, liquor at crime scenes, counterfeit materials, seal inks and drugs. Forensic applications of SR-XRF include identification of fluorescent compounds sometimes used in Japan to trace criminals, different kinds of drugs, paint chips and gunshot residues. Subchapter 7.5 deals with developments in electron-induced XRS that have mainly an impact on environmental research, namely the speciation and surface analysis of individual particles, and is written by I. Szaloki (Physics Department, University of Debrecen, Hungary), C.-U. Ro (Department of Chemistry, Hallym University, Chun Cheon, Korea), J. Osan (Atomic Energy Research Institute, Budapest, Hungary) and J. De Hoog (Department of Chemistry, University of Antwerp, Belgium). In e.g. atmospheric aerosols, it is of interest to know the major elements that occur together in one particle, i.e. to carry out chemical speciation at the single particle level. These major elements are often of low atomic number, like C, N and O. In EDXRS, ultrathin-window solid-state detectors can measure these elements but for such soft X-rays, matrix effects are enormous and quantification becomes a problem. Therefore an inverse MC method has been developed which can determine low atomic number elements with an unexpected accuracy. To reduce beam damage and volatilisation of some environmental particles, the use of liquid-nitrogen cooling of the sample stage in the electron microprobe has been studied. Finally, irradiations with different electron beam energies, i.e. with different penetration power, have been applied, in combination with the MC simulation, to study the surface and core of individual particles separately and perform some depth profiling. The given examples pertain to water-insoluble elements in/on individual so-called Asian dust aerosol particles, nitrate enrichments in/on marine aerosols and sediment particles from a contaminated river.

REFERENCE
