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Introduction

X-ray spectrometry has been known as a method for element analyses for more than 70 years and can be regarded as a routine method since the 1960s. This means that there is a broad range of instruments available, and numerous analytical tasks are carried out routinely by X-ray fluorescence (XRF) analysis. For example, XRF is used for the characterization of metallic or geological materials or for analyses of solid or liquid fuels despite the fact that other elemental analytical methods have been developed and are readily available for these applications. Among them are optical emission spectrometry with excitation both by sparks and by inductively coupled plasmas and mass spectrometry. The high importance of using XRF is due to the fact that one can achieve very high precision over a wide concentration range. XRF also requires little effort with sample preparation and the method can be automated.

Especially in the last 15–20 years, XRF has experienced a new boom mainly because the technology has further developed, and new fields of applications could be opened up. These include, among others, the analysis of layered materials and high-resolution position-sensitive analysis. This was made possible by the availability of new components for X-ray spectrometers.

The development of high-resolution energy-dispersive detectors with good count rate capability now allows precision measurements also with energy-dispersive spectrometers. The simultaneous detection of a wide energy range over a large solid angle made possible with these detectors allows not only short measuring times but also special excitation geometries. It is therefore now possible to achieve higher sensitivities in the detection of traces; further, the fluorescence radiation of small surface areas can be detected with sufficient intensity.

The development of various X-ray optics allows shaping of the primary X-ray beam and thus the concentration of high excitation intensity on small sample surfaces; this development was the key to opening up new applications in the field for a spatially resolved analysis.

These developments have significantly expanded the range of applications of XRF analysis.

However, the most important influence in the further development of XRF into a routine method was the advances in data processing technology. These made it

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possible to automate instrument control as well as the evaluation of measurement data. Not only was it possible to reduce subjective influences by a manual operator but also the processes during instrument control and measurement data acquisition could largely be automated and made more effective. The evaluation of the measurement data, such as the peak area calculation in case of overlapping peaks, or the calculation procedures for the quantification could be expanded and significantly refined by the available computing power.

These improvements have been particularly important because X-rays strongly interact with the sample matrix, which requires complex correction procedures. Nevertheless, in contrast to other analytical methods, the physics of these interactions is very well understood and can be exactly modeled mathematically. Consequently, in principle, standard-less analysis is possible, which again requires a high computing effort.

As a result of these developments, new methodical possibilities for XRF emerged, combined with an expansion of their field of applications. For this reason, it seems to be meaningful to carry out an up-to-date compilation of the applications currently being processed by XRF, in combination with a discussion of both the necessary sample preparation and instrument-related efforts and the achievable analytical performance. There are several very good books available, which however, due to their date of publication, have not been able to take into account the developments of the last 15–20 years (Erhardt 1989; Hahn-Weinheimer et al. 2012) or they do not adequately address frequently used routine applications, in particular in industrial analyses (Beckhoff et al. 2006; van Grieken and Markowicz 2002).

The goal of this book is to focus on the practical aspects of the various applications of XRF. This leads to the discussion of the requirements necessary for the analysis of the very different sample qualities, such as the type of sample preparation, the available measurement technique or the required calibration samples, as well as the type and quality of the results to be expected with these efforts. This appeared to be important, in particular, because XRF is often used in many laboratories, but methodical studies are carried out only in very few of them.

This leads to the application aspects often not being understood very well. Consequently, the analytical results are accepted without scrutinizing the influence of sample state, preparation methods, and measurement parameters. This becomes especially true because complete results are often available as the outcome of an instrumental analysis and their quality cannot be correctly comprehended.

In order to assure the quality of the applications and their results, the analyst must critically question all aspects of the test method. For this purpose, a basic understanding of the influences of sample condition, preparation methods, measurement parameters, and evaluation models used on the quality of the analytical result is imperative.

Therefore, we are deliberately focusing on the daily laboratory work with commercially available instruments. On the other hand, the interesting but not routine applications of the method utilizing synchrotron radiation excitation are not addressed. Nevertheless, methodical developments obtained on a synchrotron are often incorporated into laboratory analysis, such as micro-X-ray fluorescence (μ-XRF) or applications with grazing beam geometry. However,

this book treats only laboratory applications. If any of these newly developed methods have been implemented into special laboratory instruments these are also presented as examples.

Despite the focus on the various applications, a brief introduction to the fundamentals of X-ray spectrometry and a comprehensive presentation of the basic steps for a complete analysis are required in order to be able to relate in the following discussion of the individual applications.

The book therefore starts with a discussion of the analytical capability of X-ray spectrometry in Chapter 2. The most important relations that describe the generation of the characteristic radiation are presented, and the individual steps in the execution of an analysis follow, along with a brief characterization of their influence on the analysis result. Deeper descriptions of the physical bases are comprehensively given in other publications (e.g. Erhardt 1989; Hahn-Weinheimer et al. 2012; van Grieken and Markowicz 2002; Beckhoff et al. 2006).

In Chapter 3, the various sample preparation procedures typical for X-ray spectrometry are presented and their influence on the precision and trueness of the analyses is discussed. Even though the sample preparation is generally regarded as being very simple for XRF, it is important to carry it out carefully, appropriate to the expectations of the analysis result.

In Chapter 4, the different types of X-ray spectrometers are discussed. On the one hand, the general differences and application characteristics of wavelength-dispersive and energy-dispersive instruments are examined; on the other hand, the different instrument types as well as the instruments currently available on the market are presented.

In Chapter 5, the essential steps for the measurement of a spectrum are reviewed, in particular, the optimum selection of the measurement parameters and the steps for the evaluation of the measured data. The first step is the determination of the intensities of the fluorescence peaks, where different procedures are used for wavelength- and energy-dispersive spectrometers. Then quantification models and factors concerning the consideration of matrix interaction, both in the analysis of homogeneous samples and in the characterization of layers, are presented. Here, a comprehensive and detailed description of the theory of X-ray spectrometry is not required, since a series of detailed papers are available (see, for example, Hahn-Weinheimer et al. 2012; Jenkins et al. 1981; Lachance and Claisse 1994; Mantler 2006) and only very few new ideas have been added in the last few years. In this chapter, further possibilities for the evaluation of spectra are presented, in which the individual spectral components are not considered separately, but the spectrum as a whole is evaluated by means of chemometric methods.

Chapter 6 is devoted to the discussion of the classification, determination, and evaluation of errors. The achievable analytical precision of XRF is determined by the errors. In addition to the traditional treatment of errors with the Gaussian error model, the principle of measurement uncertainty is also discussed. This chapter is intended to qualify the expectations of an analytical result.

In Chapters 7 and 8, a brief comparison is made with other element analysis methods, in particular atomic absorption and emission spectrometry as well as mass spectrometry. The fundamentals of radiation protection when dealing with

X-ray radiation, in particular when carrying out X-ray analysis experiments, are compiled as well.

Based on these fundamentals, various applications of XRF, which have been used already over a long time period or were introduced recently, are presented and discussed. The presentation here is carried out according to the different sample qualities or according to the analytical question.

Typical XRF applications are discussed first. Chapter 9 discusses the analysis of homogeneous solid samples, such as various metallic materials, glasses, or plastics. Chapter 10 describes the investigation of powdered samples, such as geological samples, soil, building materials, slags, and dusts.

In Chapter 11, the different possibilities for analyzing liquids are presented, either by direct analysis or, for example, by different enrichment procedures to answer specific analytical questions. Applications with total reflection XRF (TXRF) are dealt with in Chapter 12. Here, in addition to ultra-trace analyses of liquids the analysis of very small sample quantities is the focus.

Descriptions of the analysis of nonhomogeneous materials cover a wide range of analytical questions. This concerns inhomogeneities normal to the sample surface, i.e. the characterization of layered materials (Chapter 14) along with their different applications, as well as inhomogeneities in the sample plane and the analysis of irregularly shaped samples (Chapter 15). In this case, only small sample areas are to be analyzed, which means a point analysis has to be carried out. This is important when identifying particles or inclusions as also when analyzing inhomogeneous materials.

Handheld instruments are increasingly being used for element analysis. Based on this fact, the applications that up to now have been typical for this instrument technology are presented in Section 15.4. It was possible to increase the efficiency of this type of instruments significantly in recent years due to the miniaturization of all hardware assemblies. In this way, their range of measurement applications could be expanded continuously. An important factor for that expansion is the possibility for "on-site" analysis, i.e. materials for analysis are no longer required to be taken to a laboratory. However, the quality of the analyses is not as high, mainly because of a very simplified or even completely missing sample preparation, undefined sample geometry, or contamination in the measuring environment.

A further important field of application of spatially resolved analysis, the determination of element distributions, is dealt with in Chapter 16. This method allows not only the analysis of small areas on structured materials, but also the investigation of their element distributions and therefore their more detailed characterization. Presentation of the examples for the distribution analysis is carried out according to the different analytical tasks. For example, the analysis of geological samples and of electronic assemblies as well as homogeneity tests of reference samples is presented.

A specific problem is the analysis of archeological objects, because they cannot be modified by preparation due to their uniqueness. Examples for such analytical tasks are discussed in Section 16.5.

In Chapter 17, special applications of the XRF analysis are described. This implies the high-throughput analysis (HTS) for the characterization of

small sample quantities, chemometric spectral evaluation with the resulting possibilities for material characterization, as well as speciation analysis.

Chapter 18 presents the requirements and conditions for the use of the XRF in process analysis, with particular attention to the automation of sample preparation. Requirements and possibilities of automated analyses are given, but the associated problems are pointed out as well.

Finally, in a brief discussion in Chapter 19 the assurance of the quality of analyses by means of a corresponding quality management system in test laboratories and also the requirements for the validation of test methods are mentioned.

All these applications are intended to demonstrate the wide range of possible measurement applications of XRF as well as the analytical performance that can be achieved.

At the end of the book, in Appendix A numerical data required for X-ray spectrometry is compiled in a comprehensive set of tables, and in Appendix B important references with information on instrument manufacturers, basic literature for the field of XRF spectrometry, important websites, as well as magazines, standards, and laws that help readers quickly find the right information and contacts for solving their analytical tasks can be found.