Vivek Kumar Singh *Editor*

X-Ray Fluorescence Spectroscopy and Chemometrics

Instrumentations, Techniques, and Applications

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To my parents, Dr. Markandeya Singh and Mrs. Chandratara Devi, who planted the seed of knowledge in my mind and lovingly nurtured it to flourish.

—Vivek Kumar Singh

Foreword

Dr. Singh has for more than 15 years applied different analytical spectroscopy methods to analyze different biological specimens. His results are published in international journals and as book chapters. In this book, Dr. Vivek Kumar Singh brought together a distinguished group of researchers with extensive expertise in *X-Ray Fluorescence Spectroscopy and Chemometrics: Instrumentations, Techniques, and Applications*. The result is a timely and comprehensive overview of the current state of the art in these analytical techniques—ranging from recent methodological advancements to a wide array of practical applications.

X-ray fluorescence, known for its non-destructive nature and inherent multi-elemental capabilities, is a highly versatile technique adaptable to numerous scientific disciplines. This book showcases several of these fields, offering diverse perspectives on how XRF is applied under varying analytical conditions.

By combining theoretical depth with real-world case studies, this collection provides a thorough and insightful exploration of modern XRF applications. It serves as a valuable resource for researchers, practitioners, and students seeking to deepen their understanding of this well-established and continually evolving analytical method.

June 2025

Professor Emeritus Johan Boman
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Foreword by Revenko and Maltsev

X-Ray Fluorescence (XRF) spectrometry is a widely employed analytical method valued for its rapid, non-destructive analysis, and its ability to determine elemental compositions across various sample matrices. Its applications include environmental monitoring, materials characterization, metallurgy, archaeology, and quality assurance. Despite its versatility, the complexity of spectral data—often featuring overlapping peaks, matrix effects, and background noise—poses significant challenges for accurate quantitative analysis.

Chemometrics is an interdisciplinary science that employs methods commonly used in data science disciplines such as multivariate statistics, applied mathematics, and computer science to solve problems in chemistry, analytical chemistry, biochemistry, chemical engineering, biology, and medicine. The development of chemometric methods also contributes to the enhancement of analytical equipment and methodologies. The number of annual publications applying chemometric techniques to resolve various issues in XRF analysis is continually increasing. Since 1980, specialized journals dedicated to chemometrics have been published. These include, for example, the *Journal of Chemometrics*, *Chemometrics and Intelligent Laboratory Systems*, and the *Journal of Chemical Information and Modeling*. These journals focus on fundamental and methodological research in the field of chemometrics. Additionally, numerous practical applications of chemometric methods are published in journals related to analytical chemistry, such as *Spectrochimica Acta Part B: Atomic Spectroscopy*, *Analytical Chemistry*, *Journal of Analytical Atomic Spectrometry*, *Applied Spectroscopy*, and *Analytica Chimica Acta.*

Chemometrics, which integrates statistical, mathematical, and computational methods, has become an essential complement to XRF spectrometry. Techniques such as multivariate calibration, principal component analysis (PCA), partial least squares regression (PLS), and advanced machine learning algorithms have been increasingly adopted to enhance data interpretation, correct spectral interferences, and improve analytical accuracy. Recent studies demonstrate that these approaches significantly increase the sensitivity and robustness of XRF analysis, especially in complex matrices and at trace levels. The integration of chemometric techniques enables the correction of matrix effects, noise reduction, and feature extraction, broadening the applicability of XRF to new challenging contexts such as environmental pollutant detection and microanalysis. With the advent of machine learning and artificial intelligence, newer algorithms like support vector machines (SVM), random forests, and neural networks have shown superior performance in spectral classification and quantification tasks. Chemometric methods and models are used to address problems of qualitative and quantitative analysis in the field of chemometrics over the past 20 years and explores the possibilities for the development. Unfortunately, we could not find a textbook among publications on chemometrics that clearly outlines the fundamental principles (methods) of chemometrics along with examples of their application in XRF practice. The published book partially fills this gap.

This book "*X-Ray Fluorescence Spectroscopy and Chemometrics: Instrumentations, Techniques, and Applications*" edited by Dr. Vivek K. Singh provides a comprehensive overview of the fundamental principles and recent advances in WDXRF, EDXRF, TXRF, and SRXRF methods, as well as X-ray detectors and the application of chemometrics to XRF spectrometry. Emphasizing recent methodological developments, practical applications, and future directions, it aims to assist researchers in optimizing their analytical workflows through advanced chemometric strategies. Although the book offers only a limited number of examples demonstrating the integration of XRF and chemometrics, its approaches can be broadly extended to other similar samples and studies. In conclusion, it is important to highlight the diverse geographic contributions of the authors involved in this collective work. Participants include colleagues from India (who contributed to six chapters), Nigeria (four chapters), Turkey (three chapters), and Slovenia (two chapters). Representatives from seven countries—Algeria, Brazil, Egypt, Spain, Cuba, Portugal, and Russia—each contributed one chapter. Some chapters, such as chapters 1, 6, and 15, were prepared collaboratively by authors from multiple countries.

This book is designed as a valuable resource for graduate students, research scientists, and other users. We hope it will find a prominent place in the libraries of every laboratory engaged in X-ray fluorescence analysis.

June 2025

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Preface

X-ray fluorescence (XRF) spectroscopy is a valuable tool in environmental studies for identifying the elemental composition of soil, sediments, water, and air samples for pollutants and contaminants. It is used to monitor air quality, analyze heavy metals in water sources, and determine the elemental composition of various environmental samples. During the past decade, XRF spectrometry has gone through major changes in the field of environmental sciences. This book is a guide which provides an up-to-date review information of XRF spectrometry for the researchers working in the field of plant science, environmental science, environmental toxicology, and geological science. It covers the basic fundamental principles, latest instrumentation developments, data analysis tools and chemometrics in X-ray fluorescence for applications in different field of science and technology. Data analysis methods and chemometrics in XRF is an excellent approach to solve qualitative and quantitative problems in XRF analyses. This book includes the practical exploration of the use of advanced chemometric methods to XRF cases in environmental science. It provides a concise guide to solve commonly encountered problems involving XRF-based spectro-analytical techniques and their applications.

The chapters are contributed by independent groups from different countries, Algeria, Brazil, Cuba, Egypt, India, Ljubljana, Nigeria, Portugal, Russia, Spain, and Turkey. Four chapters are contributed by the members of editorial advisory board of the journal “X-Ray Spectrometry” from John Wiley & Sons, and Spectrochimica Acta B, from Elsevier.

The book consists of 17 chapters. Chapter 1 covers the introduction, latest developments and applications of XRF spectroscopy. Chapter 2 highlights the recent developments particularly in WDXRF and EDXRF spectroscopy. The instrumentation, analytical performance, and emerging applications have been covered thoroughly. Chapter 3 provides a detailed discussion on gas-filled detectors, scintillation and semiconductor detectors and associated imaging applications. Chapter 4 highlights the principles of SXRFI, its applications, and recent technological developments shaping its future in scientific research. Chapter 5 discusses the recent developments in TXRF spectroscopy and applications. Chapter 6 presents a comprehensive overview of a myriad of studies utilizing chemometrics and XRF to prove the worthiness of the combination of XRF with chemometrics which may open new interesting applications of XRF in many different fields in the near future. Chapter 7 describe the review of the current tools and future trends used to statistically process data previously collected through XRF devices in the field of environmental toxicology. This chapter equally addresses the main advantages and disadvantages of techniques. Finally, newer mathematical models whose preliminary results denote an auspicious future, namely, recurrent, deep, and convolution neural networks-based algorithms, are described here and properly framed in the environmental toxicology field. Chapter 8 discusses recent advancements in the application of XRF in plant biology with an emphasis on the element distribution in plant organs by benchtop µ-XRF systems. In addition, it also addresses the challenges in sample preparation, quantification methods, and the analysis and interpretation of complex data sets. Chapter 9 explores the application of XRF for analyzing vegetation tissues. Chapter 10 explores the application of XRF in agriculture, with a particular focus on its use for measuring contamination and the integration of chemometric tools to enhance the accuracy and interpretability of the results. Chapter 11 explores the principles and applications of XRF spectroscopy in food analysis, emphasizing its advantages and limitations. Chapter 12 intends to delineate the multivariate approaches being used in the field of XRF analysis for geological samples. Chapter 13 includes the technological developments and expanding applications TXRF. Chapter 14 highlights the potential application of XRF for detection of the toxicity of fluorine, chromium, arsenic, cadmium, mercury, lead, and uranium in drinking water. In continuation, Chapter 15 gives the overview on the different XRF methods for detection of chemical hazards in drinking water. Chapter 16 provides to inform the reader about the recent studies and applications about the detection of atmospheric chemicals by XRF along with possible future studies. Chapter 17, which is the last chapter of the book, explores the application of WDXRF in diagnosing nematode-induced damage in crops, demonstrating its potential to enhance food security while promoting environmentally friendly farming approaches.

I would like to take this opportunity to express our gratitude to all of the authors for their excellent contributions in this book. We hope the readers will enjoy this book “*X-Ray Fluorescence Spectroscopy and Chemometrics: Instrumentations, Techniques, and Applications*” and that it contributes to the continued instrumental developments of XRF and environmental applications. We also hope that it encourages and inspires the beginners to the field in exploring the multifaceted aspects of XRF.

Finally, the critical evaluations and recommendations by the reviewers for the applicability of the XRF methods to environmental samples will make this book a valuable asset for anyone employing or improving upon these techniques.

Lucknow, India Vivek Kumar Singh
June 2025

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X-Ray Fluorescence Spectroscopy: Introduction, Latest Developments and Applications

1

Neslihan Ekinci, Ahmet Furkan Ekinci, Yasser Rammah,
Neha Sharma, and Vivek K. Singh

Abstract

One of the most popular and straightforward methods for non-destructive multi-element material analysis is X-ray fluorescence (XRF) spectroscopy. In the last few years, the method has advanced remarkably and shown to be helpful in several disciplines, including geology, environment, materials science, and archaeology. The technique has proven successful in industry in addition to research applications, particularly in preserving the purity of ultra-pure grade chemicals, reagents, and products. These practical applications of XRF provide a wealth of knowledge and understanding for scientists and industrial users. Due to recent developments in science and technology, we decided to compile this section as a resource that provides sufficient information for scientists and industrial users to design and set up modern XRF experiments for use in a wide range of practical applications. This compilation aims to keep you updated and aware of the latest advancements in XRF. We have also briefly discussed the application of machine learning and artificial intelligence which has the potential to expand the capabilities of XRF analysis.

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1.1 Introduction: X-Ray Fluorescence Spectroscopy

X-ray fluorescence (XRF) analysis is a widely used multi-element analysis technique with numerous practical applications, especially for non-destructive procedures. Over time, steady improvements have been observed in XRF, methodologically and instrumentally.

Recent technological advancements, such as tabletop instruments utilizing innovative low-power micro-focus tubes, new X-ray optics and detectors, and simplified access to synchrotron radiation, have revolutionized XRF. These advancements have enabled XRF to expand to include low Z elements and the acquisition of two- and three-dimensional data from a sample at a micrometer-scale. For example, developing portable equipment has facilitated more versatile use of XRF in various new contexts, including archaeometry and process control. These developments have significantly improved XRF's accuracy, speed, and versatility, making it an indispensable tool in a wide range of industries.

XRF spectroscopy is the most effective method for analyzing materials' qualitative and quantitative composition. There are two types of XRF methods: wavelength-dispersive XRF (WDXRF) and energy-dispersive XRF (EDXRF). Both methods have advantages and disadvantages. WDXRF offers a comprehensive, high-resolution examination of specific elements, especially in more complex matrices, while EDXRF is suitable for rapid and flexible analysis of various samples. So, both EDXRF and WDXRF are required for many different industries. In EDXRF, trends include miniaturization, development, and optimization of high-resolution room-temperature detectors and extension of the application range for determining light elements.

The status of WDXRF spectrometers is as follows: these spectrometers have gained popularity in recent years due to technological advancements that have increased their sensitivity, accuracy, and speed. The demand for elemental analysis with high sensitivity and reliability is one of the main reasons for the rise of the WDXRF market. Furthermore, stringent industry safety and quality assurance guidelines have significantly increased the demand for WDXRF spectrometers. So, the growth of WDXRF spectrometer trends is primarily driven by advancements in analytical technologies, raising awareness of quality control, and increasing demand from end-user industries. The key trends in the WDXRF market include incorporating automation and software solutions for advanced data processing and reporting, as well as developing portable and benchtop devices to meet a wide range of application needs.

Another significant trend is the ability of WDXRF spectrometers to provide accurate analysis of complex samples. However, these WDXRF trends are constrained by factors such as the high initial costs of the equipment, the need for skilled operators, and competition from alternative technologies such as EDXRF.

1.2 Principle and Instrumentation of EDXRF

As seen in Fig. 1.1, an EDXRF system comprises the following fundamental functional parts: a multichannel pulse height analyzer, sample chamber, Si(Li) detector, preamplifier, main amplifier, and an X-ray excitation source. The characteristics and capabilities of an EDXRF system vary depending on the electronics and computer upgrades.

Identifying characteristic lines in EDXRF is accomplished by utilizing detectors that directly measure photon energy. In its most basic form, photo absorption ejects an electron from an atom of the detector material. The loss of energy of this newly formed primary electron causes a shower of electron–ion pairs in a proportional counter, visual excitations in a scintillation counter, or showers of electron–hole pairs in a semiconductor detector. Unlike wavelength dispersion, which uses a crystal's Bragg reflecting characteristics to disperse X-rays at different reflection angles based on their wavelengths, the resulting detector signal is proportional to the original photon's energy. Although energy-dispersive detectors have lower energy resolution than wavelength-dispersive analyzers, they may detect many energies simultaneously. The most common EDXRF detector is the silicon semiconductor detector, which can achieve outstanding energy resolution.

The two alternative types of detectors discussed above, with their lower energy resolution, are limited to particular scenarios in which specific semiconductor properties are unacceptable. The germanium semiconductor detector is disadvantageous compared to traditional XRF because it can obscure other lines of interest due to escape peaks from powerful signals.

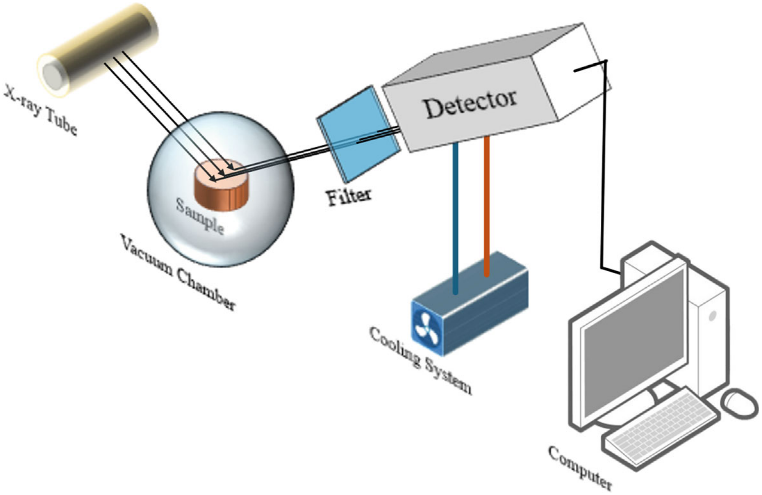

Fig. 1.1 The essential components of the EDXRF spectrometer

EDXRF spectrometers can be divided into spectrometers with 2D and 3D optics [3–7]. Both types have a source and an energy dispersive detector, but the difference is found in the X-ray optical path. For 2D spectrometers, the X-ray path is in one plane, so in 2 dimensions. For the 3D spectrometers, the path is not limited to one plane but involves 3 dimensions.

1.2.1 EDXRF Spectrometer with 2D Optics

EDXRF spectrometers with 2D optics position the X-ray tube, sample, and detector within the same plane. This is also known as direct excitation geometry which allows for simpler beam paths and direct interaction between the X-rays and the sample. 2D optics are generally used in benchtop EDXRF instruments [3–7]. This configuration facilitates a straightforward path for the X-ray beam to interact with the sample and for the emitted fluorescence to be detected. This configuration is simple and enables more compact instrument as compared 3D optics setup and are well-suited for analyzing various sample types, including liquids, powders, solids, and bulk materials. These spectrometers are widely used in industries such as metals and alloys manufacturing, petrochemicals, forensics, food analysis, and environmental analysis. Many benchtop EDXRF instruments utilize 2D optics, offering a compact and accessible solution for elemental analysis. Some 2D instruments, such as those using polarized X-rays, can achieve high sensitivity for specific elements like sulfur, phosphorus, and chlorine in petrochemicals.

1.2.2 EDXRF Spectrometers with 3D Optics

EDXRF spectrometers with 3D optics directs primary X-rays to a secondary target and then to the sample, enabling the complete elimination of primary radiation and resulting background noise when the reflections are at exactly 90° [3, 4, 7]. This enhances the peak-to-background ratio, allowing for the detection of low elemental concentrations.

This geometry involves a 3D arrangement where the X-ray tube, secondary target, and sample are in one plane, while the detector is in a perpendicular plane. The primary X-rays are first directed to a secondary target, and then to the sample, effectively creating a 90° reflection path. When the reflections are at exactly 90°, the primary X-rays that contribute to background noise are eliminated, improving the signal-to-noise ratio and allowing for more accurate analysis of lower elemental concentrations. EDXRF instruments with 3D optics are particularly useful for analyzing samples with complex matrices, where background reduction is crucial, and for detecting trace elements.

1.3 Principle and Instrumentation of WDXRF

The experimental setup of WDXRF is shown in Fig. 1.2, which consists of a (i) X-ray source; (ii) primary filters; (iii) collimators; (iv) analyzing crystals; (v) detectors, and (vi) electronics and data acquisition systems.

In WDXRF spectrometers the analyzing crystal acts as a monochromator that selectively transmits the characteristic X-rays of particular wavelength produced by the sample elements to the X-ray detector. When the emitted X-ray radiations of different wavelengths fall into the analyzing crystal at a certain angle, the diffraction pattern has been observed only for those radiations that satisfy Bragg's law (Fig. 1.3):

$$n.\lambda = 2d.\sin\theta$$

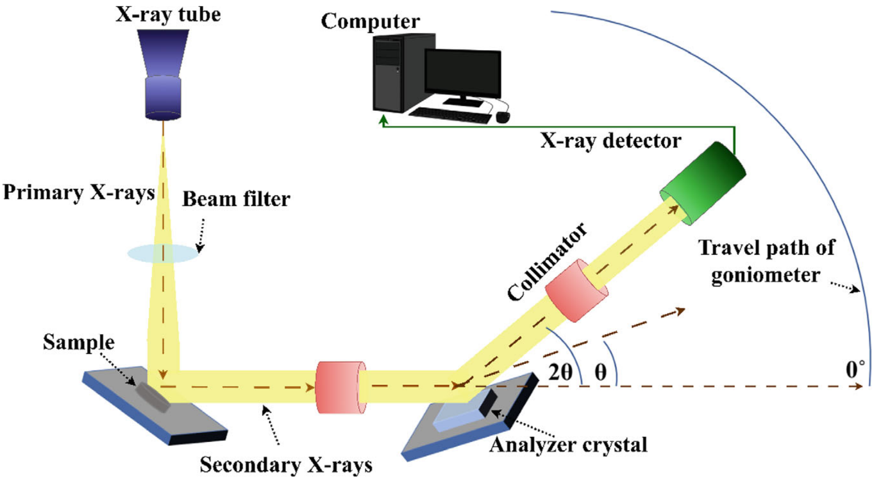

Fig. 1.2 The essential components of the WDXRF spectrometer

Fig. 1.3 Representation of Bragg's law

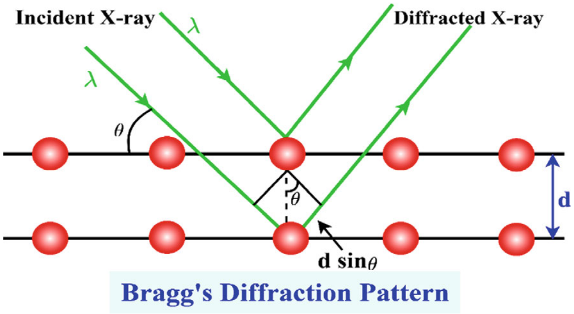

Table 1.1 List of some analyzing crystals generally used in WDXRF spectrometry system

S. no.	Crystal	Reflection plane	2d(nm)	Element range	Reflectivity
1	Lithium fluoride (LiF)	(420)	0.180	Ni-U	Average
2	Lithium fluoride (LiF)	(220)	0.284	V-U	High
3	Lithium fluoride (LiF)	(200)	0.402	K-U	Very high
4	Germanium (Ge)	(111)	0.653	P, S, Cl	High
5	Indium antimonide (InSb)	(111)	0.748	Si	Very high
6	Penthaerythritol (PET)	(002)	0.874	Cl–Al	High
7	Ammonium dihydrogen phosphate (ADP)	(101)	1.064	Mg	Low
8	Thallium (I) hydrogen phthalate (TIAP)	(1010)	2.575	Mg–O	Medium
9	Ethylene diamine-D-tartrate (EDDT)	(020)	0.880	Lighter elements	High
10	Potassium hydrophthalate (KHP)	(1010)	2.64	Mg, Na, F	High

where d denotes the interplanar distance between the lattice spacing of the crystal (*nm*), n is the order of reflection, and 'θ'is the diffraction angle.

The diffraction pattern may be obtained for different wavelengths by changing the value of 'θ' (angle of diffraction) which can be done by rotating the crystal with respect to the emitted X-ray radiation. Consequently, only X-rays with specified wavelengths will reach the detector. Some analyzing crystals that are generally used in WDXRF are listed in Table 1.1.

1.4 Comparison of EDXRF with WDXRF

1.4.1 Resolution

It describes the width of the spectral peaks. The lower the resolution, the easier to distinguish an elemental line from adjacent X-ray line intensities. The resolution of a WDXRF system is determined by the crystal and optical design, particularly collimation, spacing, and spatial reproducibility. The effective resolution of a WDXRF system can range from 20 to 5 eV. The effective resolution of a suitable

WDXRF system is 5 eV or less. In these systems, the resolution is not detector-dependent. The detector resolution determines the resolution of an EDXRF system. For example, these resolution values can be 150 eV or less for a liquid nitrogen-cooled Si(Li) detector, 150–220 eV for various solid-state detectors, or 600 eV or more for a gas-filled proportional counter. The advantage of WDXRF is its high resolution, which means less spectral overlap and lower background intensities. The advantage of EDXRF is the prohibitive cost of the WDXRF crystal and optics.

1.4.2 Spectral Overlaps

When two spectral lines overlap, it is challenging to measure them separately, so spectral deconvolution is required to determine the net intensities. When a very high resolution (low eV count) WDXRF instrument is used, most components' spectral aliasing corrections are not required. The gross intensities of each element can be calculated in a single acquisition. The EDXRF analyzer is designed to detect several components simultaneously. Some form of deconvolution technique must be applied to correct for spectral aliasing. Overlapping is no longer a problem with 150 eV resolution instruments. This is significant when compared to WDXRF. The advantage of WDXRF is that Spectral deconvolution algorithms introduce statistical counting errors for the aliasing correction of each element being corrected. This can result in a doubling or tripling of the error. Spectral aliasing becomes more problematic at lower resolutions.

1.4.3 Background

Background radiation is essential to determining detection limit, repeatability, and reproducibility.

A WDXRF instrument usually uses direct radiation flux. The background in the area of interest is directly related to the amount of continuous radiation, and the WDXRF spectrometer has the advantage due to its resolution. If a peak is one-tenth as wide, it is one-tenth as wide as the background.

An EDXRF instrument uses filters and targets to reduce the amount of continuous radiation in the area of interest.

1.4.4 Excitation Efficiency

This is the second primary factor determining detection limits, repeatability, and reproducibility. It is usually expressed in PPM per second (cps) or similar units. The relative excitation efficiency can be increased by exciting an X-ray source close to the absorption edge of the element of interest but with slightly higher energy. To excite characteristic (fluorescent) X-rays of an element in a sample, excitation of the sample with a source closer to the absorption edge of interest but with slightly higher energy can increase the relative excitation efficiency.

WDXRF generally uses direct, unmodified X-ray excitation, which contains a continuum of energies, most of which are not optimal for exciting the element of interest.

EDXRF uses filters to reduce the continuous spectrum and effectively increase the percentage of X-ray intensity above the absorption edge of the element of interest. It is also possible to provide a monochromatic line source using secondary targets to obtain the best excitation efficiency for the element line of interest.

1.4.5 Comparison of Advantages, Limitations and Recent Development Parameters of EDXRF and WDXRF

ED-XRF and WD-XRF are both X-ray fluorescence techniques used for elemental analysis, but they differ in how they separate the emitted X-rays. ED-XRF uses energy to separate the X-rays, while WD-XRF uses wavelengths. ED-XRF is known for its speed, simplicity, and portability, while WD-XRF excels in high-precision analysis and low detection limits. Table 1.2 briefly prsents the advanatges, limitations and recent develonpments and future prospects of the use of XRF technology.

In summary, the choice between ED-XRF and WD-XRF depends on the specific application and requirements. ED-XRF is ideal for quick, versatile, and cost-effective analysis, while WD-XRF excels in high-precision, detailed analysis, and low detection limits. Both techniques are continuously evolving, with new developments in instrumentation, data analysis, and application areas.

1.5 Current Interests in WDXRF and EDXRF Spectroscopy

Among the industries that EDXRF and WDXRF spectrometers are being used in the field of chemistry, forensics and environmental science, food and agriculture science, industries, life science research, material science research, semiconductor and nanotechnology, microbiology and diagnostic applications, minerals and mining petrochemicals, and pharma and biopharma industries.

1.5.1 Chemistry

Chemistry researchers are particularly interested in understanding material qualities, chemical mechanisms, and the physics underlying them.

In all fields of chemistry, EDXRF and WDXRF are valuable tools for examining material properties in both liquid and solid states. Innovations in EDXRF and WDXRF equipment are essential for advancing current research and achieving faster and more accurate results.

Table 1.2 Aadvantages, limitations, recent developments and future prospects of the use of XRF technology

Parameters	EDXRF	WDXRF
Advantages	• **Speed and Simplicity**: ED-XRF is faster and simpler to operate as compared to WD-XRF • **Versatility**: It can be used in various applications, from lab-based analysis to portable field use • **Simultaneous Multi-element Analysis**: Simultaneously analysis capability of multiple elements makes it efficient for screening	• **High Resolution**: Capability of superior spectral resolution allows for better separation of signals and accurate analysis of complex samples • **Low Detection Limits**: Lower detection limits for low-mass trace elements • **High Precision and Accuracy**: Capability of determining major elements with high precision and accuracy
Limitations	• **Lower Resolution**: ED-XRF generally has lower spectral resolution compared to WD-XRF • **Higher Detection Limits**: ED-XRF may have higher detection limits, particularly for light elements	• **Slower Analysis**: It is slower than ED-XRF, especially for analyzing a large number of elements • **Higher Cost**: More expensive due to the use of crystals and other optical components • **Limited Portability**: WD-XRF are typically larger and less portable than ED-XRF
Recent developments and future	• **Advanced Detectors**: Ongoing advancements in detector technology are improving resolution and sensitivity • **3D-EDXRF**: 3D-EDXRF with polarized X-ray beams enhances sensitivity and specificity for trace element analysis • **Miniaturization**: Miniaturized ED-XRF sensors are enabling integration into mobile platforms like autonomous drilling rigs and drones • **AI-Enhanced Analysis**: AI is being used to improve the speed and accuracy of ED-XRF analysis	• **Improved Crystals**: Synthetic thin-film multilayer crystals are being used to enhance sensitivity and resolution, especially for light element analysis • **Miniaturization**: Efforts are being made to miniaturize WD-XRF components, making them more portable • **AI-Driven Data Analysis**: AI is being used to improve data interpretation and automation in WD-XRF

1.5.2 Forensics and Environmental Science

EDXRF and WDXRF spectrometers contribute significantly to forensic and environmental science by identifying micropollutants, trace particles, and dangerous compounds. For example, identifying trace amounts of materials, hazardous chemicals, illicit substances, and explosives, as well as assisting in detecting fake paintings, significantly impacts human life.

1.5.3 Food Analysis and Agriculture

There are significant obstacles facing producers, consumers, governments, and brands due to the globalized food supply chain. Worldwide competition, the use of harmful substances in food ingredients and the strong demand for food quality control constantly increase the number of stringent regulations. EDXRF and WDXRF spectrometers protect the safety and quality of food and beverages, animal feed and agricultural products throughout the entire supply chain, from product creation to quality control in production and incoming inspections. EDXRF and WDXRF spectrometers with mobile, laboratory-based, and online systems are available to identify and quantify agents, substances, and trace elements.

1.5.4 Industrial

Today's industrial environment demands that EDXRF and WDXRF systems meet higher standards. Therefore, these analytical and quality control systems are not expected to be lower quality. The comprehensive product portfolio and innovative solutions for EDXRF and WDXRF systems must meet tomorrow's demands and help increase productivity and quality.

Precise measurements of materials and their components are required to test automotive and aerospace components under real-world conditions and help predict and prevent failure. Without sample preparation, EDXRF and WDXRF spectrometers provide spatially resolved, non-destructive material analysis (mapping) or layer thickness analysis down to trace levels.

In cement production, EDXRF and WDXRF systems are crucial in obtaining information about the chemical and mineralogical composition of raw materials and finished products, controlling and optimizing the process, and ensuring consistently high product quality. These systems provide the basis for efficient processes while ensuring cement quality and meeting international standards.

The purpose and properties of the industrial coating are of immense importance among the applications of EDXRF and WDXRF (Ekinci et al. 2001, 2006). EDXRF and WDXRF systems are used in surface refining, determining whether a product has a bioactive, photovoltaic, insular, or protective polymer coating, providing essential quality control and failure analysis.

In other words, these systems are beneficial in investigating coating properties, defects, and deterioration, especially in evaluating roughness, thickness, adhesion, homogeneity, and performance at the nanoscale and in determining the conditions under which engineers use coating.

Quality control is essential for maximizing efficiency in the highly competitive photovoltaic sector. Photovoltaic devices' efficiency, stability, and operational life have recently increased. To meet the global energy crisis, we can increase the overall optoelectronic performance of solar cells by better understanding their chemical composition, microstructure, flaws, and contaminants. This can be accomplished utilizing cutting-edge XRF (EDXRF-WDXRF).

Many semiconductor devices, including solar cells, now consist of several layers. XRF (ED XRF-WDXRF) enables simultaneous layer thickness and composition assessment to explore such layered systems in the final product.

Ceramics and glass are another industry segment. EDXRF and WDXRF systems provide comprehensive solutions for glass and ceramic analysis. We provide the necessary technologies, from chemical composition analysis of raw materials, intermediates, and finished products to spatial distribution of constituents for quality control and failure analysis of cooled samples.

Ceramics and refractors require a thorough elemental examination of raw materials, manufacturing processes, and finished products. For successful quality control and failure analysis of cooled samples, XRF analyzers provide non-destructive methods for performing spatially resolved assessments of texture and elemental distributions down to the ppm range. Typically, wavelength dispersive WDXRF is chosen because it can measure major and minor components and traces at lower concentrations. The WDXRF instruments used in this application are the S6 JAGUAR and S8 TIGER.

Different materials are mixed or dissolved in the raw glass to meet the usage requirements. XRF analysis can be performed with the EDXRF S2 PUMA or WDXRF S6 JAGUAR spectrometers for non-destructive analysis of the final glass or metallic coatings, depending on the elements and concentration ranges.

Using the wavelength dispersive spectrometer QUANTAX WDS, complex materials in the low energy or light element range can be determined better due to the excellent energy resolution and light element sensitivity.

Glasses have varying qualities depending on the application for which they will be utilized. Different mixing of various additives with raw glass can determine specific properties, such as mechanical strengths and electrical conductivities. XRF enables an exact assessment of the concentration of the components used to make a glass, allowing fine-tuning of its qualities.

One application of automated XRF is the separation of diverse types of glass for the glass recycling industry. Automated XRF instruments can accurately classify each type of glass prior to recycling.

XRF analytical systems also help the polymer industry efficiently produce high-quality plastics and develop new polymers. They are the ideal tools for simple quality control, process monitoring or research on complex materials. XRF spectrometers are also used to characterize polymers' multilayer composites, determining layer thickness and content uniformity.

XRF systems play an essential role in the research, development and characterization of new materials, raw material quality control, determination of the dynamics and kinetics of polymer reactions, and thermal stability and crystallization properties.

Life science requires the utmost accuracy in investigating various biological samples and molecular processes. Today, there are rapid and continuous changes in life science. XRF (EDXRF and WDXRF) has also found its place in this field as a new analytical instrument that allows these samples to be examined accurately with extremely high temporal and spatial resolution.

In addition, XRF analysis provides versatile, forward-thinking solutions for materials science research and testing, enabling companies to invest in process and product improvements and make continuous progress in this direction.

Due to industrial growth and technological changes, new products based on biomedical and nanotechnological materials, thin films, functional materials, carbons, or high-tech ceramics make our daily lives easier. Developing these new materials and nanostructures requires interdisciplinary collaboration in various research areas involving physics, biology, chemistry, and engineering elements.

XRF analytical systems help to produce usable products at the nanoscale. Our systems also ensure progress in efficient drug and additive production. XRF analysis offers solution-oriented approaches to any scientific problems encountered in geological sciences, mining, oil, and gas. By investigating all rocks, minerals, and materials from nanometer to planetary scale with accurate analyses, that is, by analyzing the raw materials that feed economies, it actively serves inclusive communities and humanity that support scientific discoveries.

1.6 Artificial Intelligence, Machine Learning, and Cloud Technologies: Tranforming XRF Analysis and Technology

AI, particularly machine learning (ML) and deep learning, is increasingly used to enhance EDXRF and WDXRF analysis by automating processes, improving data interpretation, and enabling real-time analysis. AI can streamline material analysis, increase accuracy, and reduce errors, ultimately boosting the efficiency and effectiveness of XRF techniques [8–11].

The application of ML models provides a better understanding of the past, as ML-enabled XRF can handle complex materials or detect trace elements [11]. XRF-ML integration has enabled the dating of French gilt bronzes, the determination of carbon in geological samples, and the identification of soil moisture levels [11].

Artificial Intelligence, Machine Learning, and Cloud Technologies are now tranforming the XRF Analysis.

A. **Automation and Streamlining**
   - **Automated Preprocessing**: AI algorithms can automatically preprocess raw XRF spectra, eliminating manual steps and reducing the time required for analysis.
   - **Feature Extraction**: AI can identify the most relevant features in the spectra, making it easier to extract meaningful information and reduce the need for manual feature selection.
   - **Data Reduction**: AI, like autoencoder neural networks, can reduce the dimensionality of XRF data, allowing for more efficient storage and processing.

B. **Improved Data Interpretation and Analysis**
   - **Pattern Recognition**: Deep learning models can learn complex patterns in XRF spectra, leading to more accurate and robust analysis.
   - **Real-Time Analysis**: AI can enable real-time analysis of XRF data, providing immediate feedback during the analytical process.
   - **Predictive Maintenance**: AI can be used to predict when XRF instruments may require maintenance, reducing downtime and improving reliability.

C. **Enhanced Accuracy and Reliability**
   - **Error Reduction**: AI algorithms can help identify and correct errors in XRF data, leading to more accurate results.
   - **Increased Reliability**: AI can enhance the reliability of XRF analysis by improving data interpretation and identifying potential issues.
   - **Improved Collaboration**: AI can facilitate improved collaboration between research groups and organizations by streamlining data processing and analysis.

D. **Specific Applications**
   - **Material Science**: AI can be used to analyze the elemental composition of various materials, including building materials, ores, and polymers.
   - **Environmental Monitoring**: AI can help assess pollution and contamination levels by analyzing XRF data from environmental samples.
   - **Cultural Heritage**: AI can aid in the analysis of materials from cultural heritage objects, helping to understand their composition and history.
   - **Medical Imaging**: AI can be used to enhance medical images, improving the accuracy and efficiency of diagnosis.

E. **Future Directions**
   - **Development of smaller and more powerful XRF instruments**: These instruments, coupled with AI and ML, will allow for more comprehensive material investigations. ML algorithms can also be used to create and implement calibrations. While traditional empirical modeling could create only material-specific calibrations, different ML models can be used in combination to improve these calibrations [11]. For example, ML-XRF analysis of archaeological ceramics can produce calibration curves with sufficient cross-validation for lighter elements like Si, Al, and Na, even when the instrument is working at higher voltage settings [11].
   - **Interdisciplinary approaches**: Combining expertise in XRF analysis, AI, and other fields will lead to significant advancements in material analysis technologies.
   - **AI-driven predictive maintenance and real-time analysis**: These capabilities will further enhance the sustainability and efficiency of XRF analysis.

1.7 Conclusion

The new developments in excitation and detection technologies render XRF benchtop spectrometers very robust. Since XRF's prominence in the geological field, EDXRF instruments are frequently used in geological samples alongside WDXRF instruments to quantify major and minor components. With the new generation databases developed, users can achieve alloy library expansion in these systems and can analyze more than 600 alloy types and more than 10,000 alloy materials simultaneously. The new parameter-fitting FP algorithm enables users to analyze metal material and element content accurately and with a low detection limit without changing mode. Both spectrometers do not damage the product during analysis, and the measurement can be conducted in extreme environmental conditions such as high and low temperatures, dust, darkness, and humidity. These spectrometers can be operated with a single button or remote control, which is very convenient. The device is also smaller and lighter, which is convenient for users to carry.

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2

Recent Developments in WDXRF and EDXRF: Instrumentation, Analytical Performance, and Emerging Applications

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Abstract

This chapter investigates recent research-driven developments in wavelength dispersive X-ray fluorescence (WDXRF) and energy dispersive X-ray fluorescence (EDXRF), focusing on instrumentation, analytical performance, and emerging applications. In WDXRF, the study critically examines the evolution of detector systems including proportional counters and scintillation detectors alongside advancements in geometrical configurations such as tube-above setups, crystal technologies, improved signal-to-noise ratios, and advanced data processing algorithms, which collectively contribute to higher resolution and precision in multi-element analysis. The chapter also explores recent trends in detector architecture and system automation that are shaping the next generation of WDXRF instruments. In the context of EDXRF, this work evaluates ongoing innovations in compact and high-throughput systems, with particular focus on cutting-edge modalities such as total reflection XRF (TXRF), grazing emission XRF (GEXRF), and micro-XRF (μ-XRF). These techniques demonstrate extended analytical capabilities for trace, ultra-trace, and spatially resolved elemental analysis in complex matrices. This chapter provides a foundation for researchers seeking to understand the instrumental evolution of XRF and its implications for future analytical research and industrial integration.

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2.1 Introduction

X-ray fluorescence (XRF) is an analytical technique extensively utilized for determining the thickness, elemental composition of materials and quality control [1–3] This method operates on the principle of high-energy X-rays or gamma rays interacting with a sample, stimulating atoms within the material to emit secondary (fluorescent) X-rays. The photon-atom interactions involve in XRF include photon attenuation, photoionization, and scattering processes such as Rayleigh, Compton, and resonant Raman scattering. XRF analysis is primarily conducted using two spectrometers: (i) wavelength dispersive XRF (WDXRF) and (ii) energy dispersive XRF (EDXRF). Both spectrometers provide comparable insights into the intensity of emitted characteristic X-rays and scattered photons, but they differ significantly in their operational mechanisms and applications. The EDXRF spectrometer utilizes a semiconductor detector coupled with a multichannel analyzer (MCA) to separate radiation wavelengths based on their energies. In contrast, WDXRF spectrometer employs crystal diffraction to isolate X-rays of interest according to Bragg’s law, $2d\sin\theta = n\lambda$, θ be the angle of diffraction. WDXRF systems analyze spectra at individual wavelengths, yielding higher intensities for specific photon energies but are limited to single-wavelength detection per scan. These distinctions highlight the complementary strengths of WDXRF for different research applications [4, 5] and offer tailored approaches to achieve precise elemental characterization [6, 7].

The instrumentation of WDXRF and EDXRF is critical for accurate and versatile across a wide range of scientific and industrial applications. In WDXRF, high spectral resolution is achieved through crystal diffraction using closely spaced X-ray wavelengths which offer superior accuracy in quantitative analysis. On the other hand, EDXRF offers rapid multi-element detection using semiconductor detectors, making it ideal for high-throughput and field applications. Additionally EDXRF caught interest of researcher due to its compact design and lower operational cost. Together, these instruments address diverse analytical requirements, from high-resolution analysis in materials research to fast and portable testing in environmental and industrial monitoring [8–11]. This chapter focuses on providing a comprehensive understanding of the instrumentation of WDXRF and EDXRF spectrometers. It delves into the principles, geometrical setups, and key components that define the functionality and performance of these systems. Additionally, recent advancements and trends in WDXRF and EDXRF technologies which enhance analytical capabilities and expand their applications in various scientific and industrial fields are discussed in the concluding section.

2.2 Instrumentation for WDXRF Spectrometer

The geometrical setup of a WDXRF spectrometer is illustrated in Fig. 2.1. The X-ray source, combined with a primary beam filter, ensures precise excitation of elements in the sample by selectively shaping the primary beam. A low-background mask changer, available in sizes such as 23, 28, and 34 mm, effectively blocks unwanted signals from the sample cup, preventing interference with the detector. A vacuum seal is incorporated between the sample chamber and the goniometer chamber, serving a critical function during sample loading. This seal remains closed during liquid sample measurements to prevent accidental spillage from damaging internal components and to conserve helium gas. It also allows the goniometer chamber to remain under vacuum while the sample chamber flushed with helium (for liquid samples) or re-evacuated.

A set of collimators is employed to enhance the resolution of the detected signals. The analyzer crystals, mounted on a crystal changer, disperse the multi-frequency fluorescence spectrum into specific wavelengths corresponding to

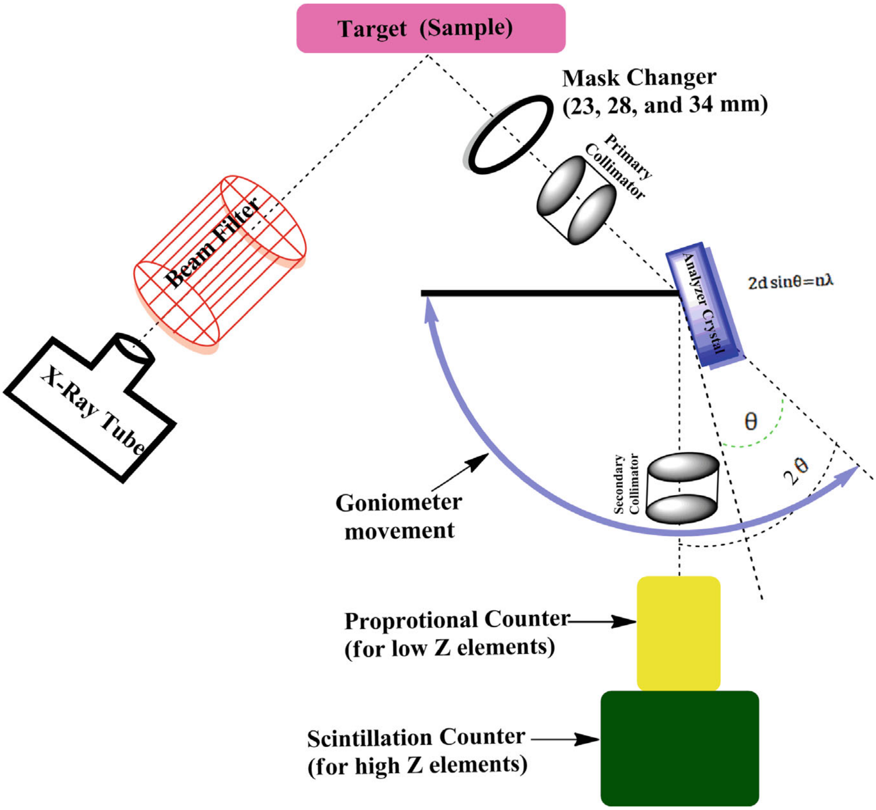

Fig. 2.1 Overview of the geometrical setup of WDXRF setup