Handbook of Practical X-Ray Fluorescence Analysis

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(Eds.)

Handbook
of Practical
X-Ray Fluorescence
Analysis

With 385 Figures and 53 Tables

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Preface

X-Ray fluorescence analysis (XRF) has developed into a well-established multi-elemental analysis technique with a very wide field of practical applications, especially those requiring nondestructive analytical methods. Over a long period of time, steady progress of XRF was made, both methodological and instrumental. Within the last decade, however, advancements in technology, software development, and methodologies for quantification have provided an impetus to XRF research and application, leading to striking new improvements. The recent technological advances, including table-top instruments that take advantage of novel low-power micro-focus tubes, novel X-ray optics and detectors, as well as simplified access to synchrotron radiation, have made it possible to extend XRF to low Z elements and to obtain two- and three-dimensional information from a sample on a micrometer-scale. The development of portable and hand-held devices has enabled a more flexible use of XRF in a variety of new situations, such as archaeometry and process control. Furthermore, synchrotron radiation provides high excitation flux and even speciation capabilities due to energetically tunable radiation.

Because of these recent advancements, the editors decided to compile a practical handbook of XRF as a resource for scientists and industrial users that provides enough information to conceive and set up modern XRF experiments for use in a wide range of practical applications. Additionally, selected sections consist of a concise summary of background information for readers who wish to gain a more in-depth understanding of the topics without conducting a lengthy search of the literature. The present handbook is not intended to be a textbook with interdependent chapters, rather a reference in which the information in each section is largely self-contained. In this way, the reader is not required to read the handbook from cover to cover, but can refer to any section without a lot of additional background.

The handbook is organized as follows. The first chapter provides a historical account of XRF and an introduction reflecting the extension of XRF to modern fields of methodology and applications. Chapters 2, 3, and 4 follow the path of a photon in an XRF instrument, originating at a source (2), being

modified by an optic (3), and registered by a detector (4). Chapter 5 deals with the various aspects of quantifying the spectra obtained from a sample by this instrument. Expert information on how to prepare the sample is the theme of Chapter 6. Chapter 7 is devoted to a variety of applications: micro-, trace, and layer analysis; environmental, geological, archaeometric, forensic, and biomedical applications; and process control. The handbook concludes with a discussion on safety regulations and useful links to physical data (Chapter 8).

We would like to take this opportunity to express our gratitude to all of the authors, especially those who completed their contributions at an early stage in the preparation of this book and patiently awaited its completion. Our thanks also go to Katherine Roegner of the Technical University, Berlin for her support in matters of language.

We hope you enjoy this practical handbook and that it contributes to the continued development of XRF. We also hope that it encourages and inspires newcomers to the field in exploring the multifaceted aspects of XRF.

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List of selected abbreviations used in the handbook

ADC	analog to digital converter
AD	Alzheimer's disease
ALS	amyothrophic lateral sclerosis
APDC	ammonium pyrrolidine-dithiocarbamate
APP	analog pulse processing
APS	active pixel sensor
APS	Argonne Photon Source
BFL	Bragg-Fresnel lens
BLR	baseline restorer
BM	bending magnet (synchrotron ID)
CAMEX	pn-CCD camera on XMM and ABRIXAS space missions
CL	cathodoluminescence
CMC	carboxymethyl cellulose
CNS	central nervous sytem
CRL	compound refractive lens
CRM	certified reference material
CVD	chemical vapour deposition
DAC	digital to analog converter
DAC	diamond anvil cell
DefMA	definition of measurement and application conditions
DL	detection limit
DPP	digital pulse processing
DSP	digital signal processing
DDTC	sodium diethyldithio-carbamate
DU	depleted uranium
EDS	energy dispersive system (spectroscopy)
EDXRS	energy-dispersive X-ray spectroscopy
EDXRF	energy-dispersive X-ray fluorescence
EDXRD	energy-dispersive X-ray diffraction
EFEM	equipment front end module
EIC	empirical influence coefficient
EMMA (*see* micro-XRF)	energy dispersive miniprobe multielement analyzer

ENC	equivalent noise charge
EPMA	electron probe micro analysis
EMPA	electron microprobe analyser
EXAFS	extended X-ray absorption fine structure
FAAS	flameless atomic absorption spectrometry
FEL	free electron laser
FET	field effect transistor
FOUP	front opening unified pods (plastic box used for wafers)
F-PC	flow proportional counter
FP	fundamental parameter
FWHM	full width at half maximum
GEXRF	grazing emission X-ray fluorescence
GPS	global positioning system
GPSC	gas proportional scintillation counter
HCA	hierarchical cluster analysis
HDAC	hydrothermal diamond anvil cell
HPGe	high purity germanium
HOPG	highly oriented pyrolytic graphite
ICP-AES	inductively coupled plasma - Auger electron spectroscopy
ICP-MS	inductively coupled plasma - mass spectroscopy
IEF	isoelectric focusing
ID	insertion device (synchrotron, e.g. wiggler, bending magnet)
IDX	4'-iodo-4'-deoxydoxorubicin (anticancer drug)
LA-ICP-MS	Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry
LOD	limit of detection
LLD	lower level of detection
MDL	minimum detection limit
MIBK	methylisobutylketone
micro-PIXE	*see* PIXE
micro-XRF (μ-XRF)	micro-X-ray fluorescence (analysis)
micro-SRXRF (also SXRF)	micro-synchrotron X-ray fluorescence
ML grating	multilayer grating
NDXRF	non-dispersive X-ray fluorescence
NaDDTC	sodium diethyldithiocarbamate
NDXRF	nondispersive X-ray fluorescence
NEXAFS	near edge extended X-ray absorption fine structure
PHA	pulse height analyzer
poly-CCC	polycapillary conical collimator
PCA	principle component analysis
PCs	principal components
PD	Parkinson's disease
PIN-diode	**p**ositive /**i**ntrinsic/**n**egative detector
PIXE	proton induced X-ray emission
pn-CCD	pn-charge coupled device

PSD	position sensitive detector
PSPC	position sensitive proportional counter
PTFE	polytetrafluorethylene
P-Z	pole-zero compensator
QXAS	quantitative X-ray analysis system (spectroscopy)
RDA	regularized discriminant analysis
REE	rare earth element
RI	refraction (refractive) index
RM	reference material
ROI	region of interest
ROSITA, XEUS, XMM, ABRIXAS	space missions of ESA
RTM	rhenium-tungsten-molybdenum composite material
SAXS	small angle X-ray scattering
SDD	silicon drift detector
SDS-PAGE	sodium dodecyl sulphate polyacrylamide gel electrophoresis
SEM	scanning electron microscopy
SEM/WDX	scanning electron microscopy/wavelength-dispersive X-ray analysis
SEM/EDX	scanning electron microscopy/energy-dispersive X-ray analysis
SIMS	secondary ion mass spectrometry
SHA	shaping amplifier
SMIF	standard mechanical interface (plastic box used for wafers)
SML	synthetic multilayer
S-PC	sealed proportional counter
SPC	statistical process control
SPE	solid phase extraction
SR	synchrotron radiation
SRXRF (SR-XRF)	synchrotron radiation X-ray fluorescence
SRXRFA	synchrotron radiation X-ray fluorescence analysis
SR-TXRF, (SRTXRF)	synchrotron radiation total reflection X-ray fluorescence
SRW	software package for synchrotrons 'SRW' developed by ESRF
STJ	superconducting tunnel junction
TIC	theoretical influence coefficient
TXRF	total reflection X-ray fluorescence
TXRFA	total reflection X-ray fluorescence analysis
TZM-anode	Mo + W anode with admixtures of Ti and Zr
VLS grating	variable line spacing grating
VPD	vapour phase decomposition
VPD-SR-TXRF	vapour phase decomposition - synchrotron radiation - total reflection X-ray fluorescence
WDXRF	wavelength dispersive X-ray fluorescence
WDS	wavelength dispersive system
WDX	wavelength dispersive X-ray analysis
XAFS	X-ray absorption edge fine structure

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XANES	X-ray absorption near-edge structure
XAS	X-ray analysis system (spectroscopy)
XPS	X-ray photo electron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRFA	X-ray fluorescence analysis
XRGS	X-ray geo scanner (geoscanner)
XSI	X-ray scanning instrument
ADP, EDDT, KAP, *PET, RAP, TlAP*	Special crystals used in X-ray diffraction and WDS: (*see* Eugene P. Bertin, Principles and Practice of X-Ray Spectrometric Analysis, Plenum Press New York 1975 (ISBN: 0-306-30809-6))

1

Introduction

T. Arai

1.1 The Discovery of X-Rays and Origin of X-Ray Fluorescence Analysis

The development of the modern theory of atomic structures was initiated based on the discovery of X-rays (1895). It was further triggered by the awareness of the existence of electrons in the atom, which was clarified by the line splitting observed when applying an external magnetic field (1896) and by the scattering of alpha particles at the atomic nucleus (1910). During the past few decades, X-ray physics has not only inspired and supported various research and development in the natural sciences, but has also had a beneficial impact on medical applications [1]. In today's civilized world, X-ray technology continues to play an important role in the advancement of material science, inspections in production processes, and diagnostics for medical treatment.

Cited below are two evolutional events in the history of X-ray science.

Watson and Crick proposed the DNA structure based on biological and structural chemistry including X-ray crystal structure analysis. Wilkins precisely studied the crystal structure using a rotating crystal method. The consolidation of their works led to the determination of the double helical structure of DNA, which has a three-dimensional structure of a screwed ladder and a regular arrangement of the four bases: adenine, thymine, guanine, and cytosine in the space between the two ladder poles [2].

The combination of the high X-ray transparency of the human body and its use for medical treatment brought about a notable advance in the use of X-rays for medical applications. Oldendorf planned to develop a relevant instrument in 1960. Then, Cormack presented his idea that included a mathematical treatment for three-dimensional imaging in 1963 and 1964. As Hounsfield used a radioactive source, a long time was required for taking a picture. Finally, he developed a computer-assisted tomogram using the consolidated technology of X-ray tube radiation, X-ray detectors, and computer calculations for the

preparation of three-dimensional pictures of X-ray intensity and indications for easy and precise diagnosis. Clinical data were presented in 1972 and 1973. Many instrumental improvements led to high-grade medical treatment that was founded on the present X-ray machine [3].

On November 8, 1895, Wilhelm Conrad Röntgen discovered X-rays in his laboratory at the physics institute of Julius-Maximilians University of Würzburg in Bavaria. He had studied cathode rays using an air-filled Hittorf-Crooks tube, which was shaded with a black paper. The tube wall was hit by electrons and emitted light. In his darkened room, he noticed a weak luminescence which radiated from a fluorescent screen located near the tube. He recognized "eine neue Art von Strahlen" (a new type of rays), which originated from the tube. After changing the experimental and surrounding conditions, he was able to observe the emission of weak rays of light on the fluorescent screen. He announced the new experimental results. It was immediately recognized that this discovery might be used to look into the structure of a living human body and the interior of constructed materials [4, 5].

After the announcement by Röntgen, two further important discoveries were made: radioactivity from uranium by Becquerel (1896) as well as radium and polonium by Marie and Pierre Curie (1898).

Using an aluminum filter method for the separation of X-rays and an ionization chamber for X-rays detection, Barkla studied the nature of X-rays relative to the atomic structure. Observing the secondary X-rays which were radiated from a target sample, he discovered the polarization of X-rays (1906), the gaps in atomic absorption (1909), and the distinction between continuous and characteristic X-rays, which consisted of several series of X-rays, named the K, L, M ... series (1911). The intensity and distribution of continuous X-rays were dependent on the number of electrons in an atom, and the characteristic X-rays were related to the electron energy configuration in the atom [6]. In succession to Barkla's works, the wave properties of X-rays were investigated by von Laue, who exhibited X-rays diffraction from a single crystal, which was composed of a three-dimensional structure with a regularly repeating pattern (1912). The experimental results showed the comparability of the wavelength of X-rays with the atomic distances and confirmed the wave properties of X-rays.

W. H. Bragg, who derived the famous Bragg's formula, was interested in von Laue's experiments. Using a Bragg spectrometer, the X-ray reflection patterns from single crystals of NaCl and KCl were observed to be the regular patterns of an isometric system showing differences in the X-ray intensity when comparing sodium and potassium. This was the starting point of crystal structure analysis with X-rays [7].

For the expansion of radiographic technology, the need for a heavy-duty X-ray tube emerged. After the tungsten filament (1908) and the tungsten incandescent lamp (1911) were invented, Coolidge developed a new type of tube setting, successfully solving the problem of low power and instabilities of

a gas-filled discharge tube. In this new tube, thermal electrons emitted from a hot filament hit the target, which was an emission source of X-rays (1913) [8].

Following the investigation of the properties of X-rays by Barkla, Moseley studied characteristic X-rays in an exchange of communications with W.L. and W.H. Bragg. He put target samples into a gas-filled discharge tube, which were then irradiated with electrons for the generation of characteristic x-rays. The narrow collimated characteristic X-rays hit the cleaved surface of a $K_4Fe(CN)_6 \cdot H_2O$ crystal and the third-order lines of Bragg reflection X-rays were obtained, which were shown in the famous photograph taken in 1913 [9]. Moseley elucidated the relationship between the characteristic X-rays and the measured elements, and communicated his experimental results to Bohr [10].

Siegbahn produced an X-ray spectrometer for a wider range of characteristic X-rays. He measured the wavelengths of characteristic X-rays precisely and classified them into α, β, γ . . . according to the X-ray intensities in the respective series. X-ray spectroscopy was established with these works (1913–1923).

In the next advances, Hadding tried to analyze rare earth elements using the X-ray method. His work was supported by Siegbahn.

Due to the establishment of the structure of atoms, it became possible to predict the existence of elements that had yet to be discovered. This was based on the assumption that undiscovered elements belonging to the same family of elements in the periodic table have the same chemical features. In this respect, hafnium was isolated by von Hevesy and Coster (1923) [11] and rhenium by Noddack and Tacke with the support of Berg (1925).

During the initial stage of the use of X-ray spectroscopy for chemical analysis, the samples being analyzed were modified (or even destroyed) when electron excitation was applied, leading to changes in the X-ray intensities. Hadding, Glocker, and Frohnmayer pointed out the analytical problems of inter-element effects in quantitative analysis. When electron excitation was used, Coster and Nishina noticed sample evaporation because of the induced heat in the sample (1925), and Glocker and Schreiber found concentration changes in the constituent elements (1928). For the emission of characteristic X-rays in X-ray spectrochemical analysis, the X-ray excitation method was adopted as a non-destructive analysis method. Although the relative distance between the X-ray source and sample was reduced to increase the primary X-ray intensity, the resultant X-ray intensity was still insufficient to be measured [12]. On the positive side background X-rays became lower and, as a result for quantitative analysis, low intensity peaks could be measured easily.

For the measurement of X-ray intensities an ionization chamber or a photographic plate had been used. Perrin invented the ionization chamber in 1896, which was used in Barkla's works and adopted in Bragg spectrometers. In 1928, Geiger and Müller produced a new useful counter for the detection of γ-rays and X-rays, called the Geiger-Müller counter. Although analytical

principles and procedures had been studied in the academic field, the development of X-ray analytical instruments for general use had to wait until the end of the Second World War.

During the Second World War, the precise measurement of the cutting angle of quartz was required in mass production of oscillation plates. For this purpose, an X-ray apparatus was built by Parrish and Gordon based on a modified Bragg ionization chamber spectrometer (1945) [13]. Based on production experiences of the X-ray apparatus, Friedman introduced detectors for γ-rays and X-rays, as well as sensing head systems for various X-ray applications (1947) [14]. Then he started to develop a prototype X-ray spectrometer for the measurement of diffracted X-ray intensities and Bragg angles. Adopting a new Geiger-Müller counter and an electronic pulse counting unit (1947), a quartz plate which was located at the rotation center of a goniometer was replaced with a solidified powder sample (1945) [15].
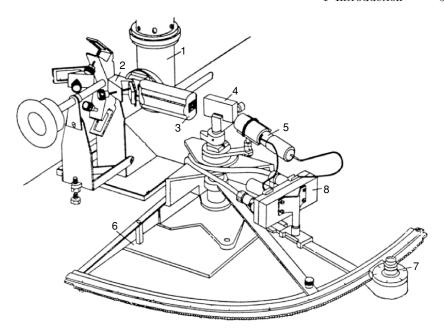
When the iron-containing samples were measured using a Cu target X-ray tube, an abnormal increase in X-ray intensity was found, because the iron fluorescent X-rays radiating from a diffraction sample had strayed into the detector. As a result of the realization that fluorescent X-rays could be detected easily by this measuring system, a new X-ray fluorescence spectrometer was built. Analytical problems of measuring weak fluorescent X-ray intensities were encountered in the 1920s and the 1930s, which changed the requirements for the improvement of instrumentation. Friedman and Birks adopted a high power X-ray tube with a large window which gave rise to an increase in the effective solid angle, contributing to a short distance between the x-ray source in the x-ray tube and the sample to be analyzed. On the goniometer that is used in X-ray diffraction measurements, a bundle of narrow nickel pipes was used for collimation. Based on the need for a large reflecting surface, high reflecting power and relatively small lattice spacing, NaCl and fluorite crystals were chosen (1948) [16]. Figure 1.1 shows the X-ray fluorescence spectrometer developed by Friedman and Birks.

Expanding upon Friedman and Birks' work, Abbott was successful in building the first commercial X-ray fluorescence spectrometer in 1948 [17]. These works can be regarded as the beginning of modern X-ray spectrometry.

1.2 Historical Progress of Laboratory X-ray Fluorescence Spectrometers

In this section, the historical progress and important developments of the wavelength dispersive method in laboratory X-ray instruments are briefly reviewed.

In 1964, Birks, one of the pioneers of the X-ray fluorescence spectrometer, visited Japan and delivered a lecture "X-ray fluorescence: Present limitations and future trends." In his lecture, the analytical limits achievable in those days were reviewed covering elements from sodium to uranium, the detectability of

Fig. 1.1. The X-ray fluorescence spectrometer by Friedman and Birks [16].
1, X-ray tube; 2, specimen holder; 3, Soller collimator; 4, crystal; 5, Geiger counter;
6, base plate; 7, vernier for setting and reading the angular position of the crystal;
8, pre-amplifier

ppm order, the analytical precision of about 1%, and the possible analytical
error caused by the matrix effects [18]. Concerning the anticipated further
progress of the analytical method, he directed attention to the measurement of
light and ultralight elements, sample preparation, improvement of excitation
and detection of X-rays, utilization of computers for spectrometer control and
analytical calculation as well as to the energy dispersive method appearing
just then.

In 1976, Birks reviewed again the principles of X-ray fluorescence analysis
and the progress of analyzing techniques including the instrumentation and
the evaluation of the new methods. In this review, he emphasized the progress
in the matrix correction method and the fundamental parameter method,
which were led by the evaluation of the X-ray tube spectrum. In addition,
some applications and future expectations were discussed [19].

In 1990, Gilfrich made a survey of X-ray fluorescence analysis. He directed
attention to the new X-ray source, namely, the synchrotron radiation and to
the introduction of synthetic mutilayers as analyzing crystals, to advanced
X-ray technologies such as TXRF and EXAFS, semiconductor detectors for
energy dispersive techniques, and to the significant progress of data handling
with small computers [20].

Furthermore, in 1997, Gilfrich [21] gave a retrospect on the historical development of X-ray analysis during the past 100 years in commemoration of the discovery of X-ray by W.C. Roentgen.

Against the backdrop of such constructive remarks and the popularization of the X-ray fluorescence spectrometer, there have been many kinds of X-ray instruments developed for various measuring purposes, so that the instruments available today have gone ahead of the prediction by Birks in terms of type and number.

An X-ray analysis system configured with a X-ray diffractometer and an X-ray fluorescence spectrometer was introduced by Parrish [22]. As both equipments were provided with a high voltage power supply for an X-ray tube and shared a pulse counting system , it was widely utilized in laboratory applications. In addition, this spectrometer was equipped with a helium attachment for measuring soft X-rays.

Spielberg, Parrish, and Lowitzsch described the functional elements of non-focusing optics and the geometrical condition for their harmonizing combinations [23]. They used a closer coupling of an X-ray tube for the sample and a large solid angle of primary X-rays for higher fluorescent intensity. Consequently, the inhomogeneity of fluorescent intensity distribution arising from the change of irradiating density of primary X-rays on the sample was brought forth. Their equipment was based on the Bragg spectrometer and had a parallel beam optics composed of a flat analyzing crystal and a double Soller collimator. Furthermore, the X-ray tube, the composed X-ray optics, and a sample container for primary X-ray irradiation were assembled in such a way as to embody convenience of use.

Arai pointed out that the total reflection from a metal sheet of a Soller collimator broadened a peak profile in its tails [24]. In addition, he studied the aberration of peak profiles caused by the vertical (the direction parallel to the goniometer rotation axis) divergence, reflection profiles from imperfect single crystals, and spectral overlapping [25].

Campbell and Spielberg, and Parrish and Lowitzsch studied a double Soller collimator on the basis of a flat crystal X-ray optics [23, 26].

Arai proposed as a practical solution that the horizontal divergence of a sub-Soller collimator should be two or three times larger than that of the main collimator, which was dependent on the grade of mosaic structure of analyzing single crystals.

For the analysis of the light elements, a helium and vacuum path spectrometer was offered by Miller and Zingaro for laboratory-use instruments [27].

An X-ray spectrometer for industrial applications, equipped with parallel beam optics and named Autrometer, was developed by Miller and Kiley in 1958. It was equipped with a step scanning goniometer, a tandem detector connecting a scintillation counter and a gas flow proportional counter, and adapted with a helium path for light element analysis. The spectrometer further incorporated the intensity ratio method designed to maintain the X-ray intensity stability upon referring to the standard sample intensity for quantitative determination [28, 29].

Equipments other than the scanning (and parallel-beam-optics) spectrometers, pursuing the basic features of rapid and high precision analysis for industrial applications, are the spectrometers equipped with multi-channel fixed goniometers.

Kemp developed the first combination model of scanning and fixed channel multi-element X-ray spectrometer based on the development and production of an optical emission spectrometer [30].

Furthermore, Jones, Paschen, Swain, and Andermann proceeded with the development of this advanced X-ray equipment, which adopted the focusing circle optical system with curved crystals, the detectors with the gas discrimination, and the direct capacitor accumulation of electric signals of the detector [31]. In order to obtain a higher intensity of measuring X-rays, focusing optics were adopted using Johann or Johansson curved crystals. In the case of the scanning goniometer, a curved single crystal moved in a straight line away from the entrance slit on the focusing circle, and then the detector slit on the focusing circle crawled along the four-leaf rose locus. The distance between the entrance slit and the curved crystal center was proportional to the wavelength of the measuring X-rays. The gas discrimination in the detector had a favorable effect on the intensity reduction of backgrounds and overlapping X-rays. The capacitor accumulation method was effective to measure a high counting rate of analyzing X-rays.

For light element analysis of cement samples, a helium path was adopted by Andermann, Jones, and Davidson [32], and then Andermann and Allen intensified the X-ray analysis of various materials related to cement industry. Additionally, a vacuum spectrometer was developed for light element analysis of cement and steel production applications by Dryer, Davidson, and Andermann [33]. In order to procure high intensity stability of the measuring X-rays and compensate the matrix effect, an X-ray monitoring method to detect scattered X-rays from the sample was introduced into the intensity measuring system by Andermann and Kemp [34]. However, the aforementioned capacitor accumulation and the monitoring method were changed to the absolute intensity measurement using pulse-counting circuits with a clock timer and the pulse selection method later.

Anzelmo and Buman presented a combined instrument which contained a scanning goniometer and several fixed goniometers in one spectrometer, in 1983 at the Pittsburgh Conference. This was a new concept of adaptable use in an analytical laboratory [35].

In 1995, Kansai, Toda, Kohno, Arai, and Wilson developed a fixed channel-multi-element spectrometer provided with 40 fixed goniometers by adopting logarithmic-spiral curved crystal monochromators. For high speed analysis, high counting rate X-ray intensity measurement of 10 to 50 million counts per second was carried out with a pure material by means of a combination of an X-ray beam attenuator and high speed electronic circuits with fast counting rate response. In the meanwhile, for the impurity analysis of various ores or high purity materials, two receiving slits located beside each other, one for

a fluorescent peak and the other for the background, were equipped in a goniometer for background correction calculation [36].

The core technology of an X-ray spectrometer consists of the excitation of fluorescent X-rays, the X-ray optics, and matrix correction calculations based on the fundamental parameter method. Described in this section are the remarkable progress and development in X-ray optics. Other features will be touched upon in the following section.

1.3 Measurement of Soft and Ultrasoft X-Rays

The purpose of conducting soft and ultrasoft X-ray measurements is to study the emission spectra influenced by chemical bonding or to make a quantitative determination of low atomic number elements. For the study of emission spectra, a high resolution spectrometer, and for quantitative determination, a high intensity one are required, respectively. The analytical problems in a quantitative determination of low atomic number elements originate from the inherent performance caused by the low excitation efficiency of soft X-rays and low reflectivity of spectroscopic device.

1.3.1 X-Ray Tubes for Soft and Ultrasoft X-Rays

In earlier days, most of the X-ray tube manufacturers supplied a side window tube with a thick beryllium window (about 1 mm thick) for spectrometer use. Inasmuch as these X-ray tubes are almost inefficient for X-ray measurement of light elements owing to the low excitation efficiency, new X-ray tubes with chromium and scandium target were developed on the basis of the side window structure by Kikkert and Hendry [37]. Characteristic K-radiation from this new tube passing through a relatively thin beryllium window can effectively excite the fluorescent X-rays of light elements.

Caldwell used a General Electric XRD 700 spectrometer equipped with a dual target (W, Cr) tube [38]. For heavy element measurement, the tungsten target, and for light element measurement like titanium and silicon in high alloy steel, the chromium target, were used, respectively. The analytical errors for titanium and silicon could be reduced. It demonstrated an improvement in the analytical accuracy of light elements by increasing the soft X-ray excitation efficiency.

Mahn of Machlett Laboratories Inc. developed an end window X-ray tube with a thin beryllium window and a rhodium target [39]. In order to minimize the secondary electron bombardment effect on the thin beryllium window, the target surface was charged with positive potential and the cathode filament was earth-grounded. The L series X-rays from the rhodium target are effective for excitation in soft and ultrasoft X-ray regions while the K series X-rays from the target are effective for heavy element analysis.

Gurvich compared various X-ray tubes and emphasized the advantage of the end window X-ray tube for light element analysis [40].