29

REQUIREMENTS FOR X-RAY FLUORESCENCE

Walter Gibson
X-Ray Optical Systems
East Greenbush, New York

George Havrilla
Los Alamos National Laboratory
Los Alamos, New Mexico

29.1 INTRODUCTION

The use of secondary x rays that are emitted from solids bombarded by x rays, electrons, or positive ions to measure the composition of the sample is widely used as a nondestructive elemental analysis tool. Such secondary x rays are called fluorescence x rays. The "characteristic rays" emitted from a solid irradiated by x rays or electrons were shown in 1913 by Moseley to have characteristic wavelengths (energies) corresponding to the atomic number of specific elements in the target. Measurement of the wavelength of the characteristic x rays, as well as observation of a continuous background of wavelengths, was made possible by use of the single-crystal diffraction spectrometer first demonstrated by Bragg. There was active development by a number of workers and by the late 1920s x-ray techniques were well developed. In 1923, Coster and von Hevesey used x-ray fluorescence to discover the unknown element hafnium by measurement of its characteristic line in the radiation from a Norwegian mineral, and in 1932 Coster and von Hevesey published the classical text Chemical Analysis by X-Ray and Its Applications. Surprisingly, there was then almost no further activity until after World War II. In 1947 Friedman and Birks converted an x-ray diffractometer to an x-ray spectrometer for chemical analysis, taking advantage of work on diffraction systems and detectors that had gone on in the previous decade. An x-ray fluorescence measurement in which the energy (or wavelength) spectrum is carried out by the use of x-ray diffraction spectrometry is called wavelength-dispersive x-ray fluorescence (WDXRF). There was then rapid progress with a number of companies developing commercial x-ray fluorescence (XRF) instruments. The early developments have been discussed in detail by Gilfrich. During the 1960s, the development of semiconductor particle detectors that could measure the energy spectrum of emitted x rays with much higher energy resolution than possible with gas proportional counters or scintillators resulted in an explosion of applications of energy-dispersive x-ray fluorescence (EDXRF). Until recently, except for the flat or curved diffraction crystals used in WDXRF, x-ray optics have not played an important role in x-ray fluorescence measurements. This situation has changed markedly during the past decade. We will now review the status of both WDXRF and EDXRF with emphasis on the role of x-ray optics without attempting to document the historical development.

∗This volume is dedicated in memory of Walter Gibson.
There are thousands of XRF systems in scientific laboratories, industrial laboratories, and in manufacturing and process facilities worldwide. Although most of these are EDXRF systems, many use WDXRF spectrometry to measure the intensity of selected characteristic x rays. Overwhelmingly, the excitation mechanism of choice is energetic electrons, and many are built onto scanning electron microscopes (SEMs). Electron excitation is simple and can take advantage of electrostatic and magnetic electron optics to provide good spatial resolution and, in the case of the SEM, to give elemental composition maps of the sample with high resolution. In general, the only x-ray optics connected with these systems are the flat or curved analyzing crystals. Sometimes there is a single analyzing crystal that is scanned to give the wavelength spectrum (although multiple crystals, usually two or three, are used to cover different wavelength ranges). However, some systems are multichannel with different (usually curved) crystals placed at different azimuthal angles, each designed to simultaneously measure a specific wavelength corresponding a selected element or background wavelength. Sometimes a scanning crystal is included to give a less sensitive but more inclusive spectral distribution. Such systems have the benefit of high resolution and high sensitivity in cases where the needs are well defined. In general, WDXRF systems have not been designed to take advantage of recent developments in x-ray optics, although there are a number of possibilities and it is expected that such systems will be developed. One important role that x-ray optics can be used in such systems is shown in Fig. 1.

In this arrangement, a broad angular range of x-ray emission from the sample is converted into a quasi-parallel beam with a much smaller angular distribution. A variety of collimating optics could be used, for example, polycapillary (as shown), multilayer, nested cone, and so on. The benefit, represented as the gain in diffracted intensity, will depend on the optic used, the system design (e.g., the diffracting crystal or multilayer film), and the x-ray energy. With a polycapillary collimator, 8 keV x rays from the sample with divergence of up to approximately 12°, can be converted to a beam with approximately 0.2° divergence. With a diffraction width of 0.2° and a transmission efficiency for the optic of 50 percent, the gain in the diffracted beam intensity for flat crystal one-dimensional diffraction would be typically more than 30. Further discussion of the gains that can be obtained in x-ray diffraction measurements can be found in Sec. 29.5. Another potential benefit from the arrangement shown in Fig. 1 is confinement of the sampling area to a small spot defined by the collection properties.

**FIGURE 1** Schematic representation of collimating optic in WDXRF system.
of the optic as discussed in Chap. 53. Scanning of the sample will then give the spatial distribution of selected elements. This is also useful in so-called environmental, or high-pressure, SEMs where the position of the exciting electron beam is not so well defined.

**Fine Structure in WDXRF Measurements**

As noted previously, most of the WDXRF systems in use involve electron excitation either in SEM systems or in dedicated electron micro-probe systems. Photon emission from electron excitation systems contains, in addition to the characteristic lines, a continuous background due to bremsstrahlung radiation resulting from slowing down of the electrons in the solid. Although this background does not seriously interfere with many measurements of elemental composition, it can limit the measurement sensitivity, and can preclude observation of very low intensity features. If the fluorescence x rays are excited by incident x rays, or energetic charged particles, the bremsstrahlung background can be avoided. It should be noted that a continuous background still is present when a broad x-ray spectrum is used as the exciting beam due to scattering of low-energy x rays. This can be largely avoided if monoenergetic x rays are used.

A dramatic illustration of the value of a low background in XRF measurements is contained in recent studies in Japan of fine structure in fluorescence spectra. Accompanying each characteristic x-ray fluorescence peak is an Auger excitation peak displaced typically approximately 1 keV in energy and lower in intensity by nearly 1000 times. This peak is not usually observable in the presence of bremsstrahlung background from electron excitation. By using x-ray excitation to get a low background and WDXRF to get high-energy resolution, Kawai and coworkers measured the Auger excitation peaks from Silicon in elemental Si and SiO$_2$ and from Al. They showed that the observed structure corresponds to x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) that has been observed in high-resolution synchrotron studies. Very long measurement time was necessary to obtain sufficient statistical accuracy. This type of measurement could presumably be considerably enhanced by the use of collimating optics as shown in Fig. 1.

**29.3 ENERGY-DISPERSIVE X-RAY FLUORESCENCE (EDXRF)**

During the 1960s, semiconductor detectors were developed with dramatic impact on energy and later position measurement of energetic charged particles, electrons, and x rays. Because of their high efficiency, high count rate capability, high resolution compared with gas counters, and their improved energy resolution compared with scintillation counters, these new detectors virtually revolutionized radiation detection and applications including x-ray fluorescence. Initially, the semiconductor junction detectors had a thin active area and, therefore, were not very efficient for x rays. However, by use of lithium compensation in the active area of the detector, it was possible to make very thick depletion layers (junctions) and, therefore, to reach a detection efficiency of 100 percent for x rays. Later, high-purity germanium was used to make thick semiconductor junctions. Such large-volume semiconductor junctions need to be cooled to obtain the highest energy resolution (typically, 130 to 160 eV).

There are now thousands of XRF systems that use cooled semiconductor detectors, most of them mounted on SEMs. Most SEM-based XRF systems do not use any x-ray optics. The detectors can be made large enough (up to 1 to 2 cm$^2$) and can be placed close enough to the sample that they collect x-rays over a relatively large solid angle.

As pointed out previously, electron excitation produces a background of bremsstrahlung radiation that sets a limit on the signal-to-background ratio and, therefore, the minimum detection limit for impurities. This background can be avoided by using x rays or energetic charged particles as the excitation source. Consequently, it is common to see cooled lithium-drifted silicon Si(Li) or high-purity germanium (HpGe) detectors mounted on accelerator beamlines for materials analysis. The ion
beam-based (usually proton or helium ion) technique is called particle-induced x-ray emission (PIXE). Again, these do not require optics because the detector can be relatively close to the sample. As with the electron-based systems, optics necessary for controlling or focusing the exciting beam are electrostatic or magnetic and will not be discussed here. When the exciting beam is composed of photons from a synchrotron or free-electron laser (FEL) source, the situation is virtually the same, with no optics required between the sample and the detector. Mirrors and monochromators used to control the exciting beam are discussed in Chaps. 39 and 44.

Monocapillary Micro-XRF (MXRF) Systems

However, if the excitation is accomplished by x rays from a standard laboratory-based x-ray generator, x-ray optics have a very important role to play. In general, the need to obtain a high flux of exciting photons from a laboratory x-ray source requires that the sample be as close as possible to the source. Even then, if the sample is small or if only a small area is irradiated, practical geometrical considerations usually limit the x-ray flux. The solution has been to increase the total number of x rays from the source by increasing the source power, with water-cooled rotating anode x-ray generators becoming the laboratory-based x-ray generator of choice. (For a discussion of x-ray sources, see Chap. 54.) To reduce the geometrical \(1/d^2\) reduction of x-ray intensity as the sample is displaced from the source (where \(d\) is the sample/source separation), capillaries (hollow tubes) have been used since the 1930s. Although metal capillaries have been used, glass is the overwhelming material of choice because of its easy formability and smooth surface. In most of the studies reported earlier, a straight capillary was placed between the x-ray source and the sample, and aligned to give the highest intensity on the sample, the capillary length (6 to 20 mm) being chosen to accommodate the source/sample spacing in a commercial instrument. An early embodiment of commercial micro x-ray fluorescence employed metal foil apertures with a variety of dimensions which created spatially resolved x-ray beams. While these crude “optics” provided x-ray beams as small as 50 \(\mu\)m, the x-ray flux was quite limited due to the geometrical constraints.

In 1988, Stern et al. described the use of a linearly tapered or conical optic that could be used to produce a smaller, more intense but more divergent beam. This has stimulated a large number of studies of shaped monocapillaries. Many of these are designed for use with synchrotron beams for which they are especially well suited, but they have also been used with laboratory sources. A detailed discussion of monocapillary optics and their applications is given in Chap. 52.

In 1989, Carpenter built a dedicated system with a very small and controlled source spot size, close-coupling between the capillary and source and variable distance to the sample chamber. The sample was scanned to obtain spatial distribution of observed elemental constituents. A straight 10-\(\mu\)m diameter, 119-mm-long capillary showed a gain of 180 compared to a 10-\(\mu\)m pinhole at the same distance and measurements were carried out with a much lower power x-ray source (12 W) than had been used before.

More recently, a commercial x-ray guide tube or formed monocapillary has been employed to produce x-ray flux gain around 50 times that of straight monocapillary. This modest flux gain enables the more rapid spectrum acquisition and elemental mapping of materials offering new spatially resolved elemental analysis capabilities at the 10 s of micrometers scale.

Polycapillary-Based MXRF

As discussed in Chap. 53, a large number of capillaries can be combined to capture x rays over a large angle from a small, divergent source and focus them onto a small spot. This is particularly useful for microfocus x-ray fluorescence (MXRF) applications.

Using the system developed by Carpenter, a systematic study was carried out by Gao in which standard pinhole collimation, straight-capillary, tapered-capillary, and polycapillary focusing optics could be compared. A schematic representation of this system with a polycapillary focusing optic is shown in Fig. 2. The x rays were generated by a focused electron beam, which could be positioned electronically to provide optimum alignment with whatever optical element was being used.
The target material could be changed by rotating the anode as shown in Fig. 2. Measurement of the focal spot size produced by the polycapillary focusing optic was carried out by measuring the direct beam intensity while moving a knife edge across the focal spot. The result of such measurements for Cu Kα and Mo Kα x rays are shown in Fig. 3.

The intensity gain obtained from the polycapillary focusing optic depends on the size of the x-ray emission spot in the x-ray generator, on the x-ray energy, and on the input focal distance (distance between the source spot and the optic). This is because the effective collection angle for each of the transmitting channels is controlled by the critical angle for total external reflection (see Chap. 53). For the system shown, the flux density gain relative to the direct beam of the same size at 100 mm from the source, is shown in Fig. 4 for Cu Kα and Mo Kα x rays. The maximum gain is about 4400 at 8.0 keV and 2400 at 17.4 keV, respectively.

A secondary x-ray spectrum obtained by irradiating a standard NIST thin-film XRF standard sample, SRM1833, is shown in Fig. 5. Zirconium and aluminum filters were used before the optic to reduce the low-energy bremsstrahlung background from the source. The flux density of the beam at the focus was calculated to be $1.5 \times 10^7$ photons⋅s⋅μm² for Mo Kα from the 12-W source operated at 40 kV. The minimum detection limits (MDLs) in picograms for 100-s measurement time were as follows: K, 4.1; Ti, 1.5; Fe, 0.57; Zn, 0.28; and Pb, 0.52. The MDL values are comparable with those obtained by Engstrom et al., who used a 200-μm diameter straight monocapillary and an x-ray source with two orders of magnitude more power (1.7 kW) than the 12-W source used in the polycapillary measurements.

By scanning the sample across the focal spot of the polycapillary optic, the spatial distribution of elemental constituents was obtained for a ryolitic glass inclusion in a quartz phenocryst found in a layer of Paleozoic altered volcanic ash. This information is valuable in stratigraphic correlation studies. The results are shown in Fig. 6. Also shown are the images obtained from Compton scattering (Comp) and Rayleigh scattering (Ray).

There are a number of commercial instruments employing the monolithic polycapillary optics to spatially form the excitation beam. Their commercial success lies in being able to generate an increase in x-ray flux 2 to 3 orders of magnitude greater than that can be obtained without the optic at a given location.
spot size. The future development and potential growth of MXRF rests with the continued innovation of x-ray optics in general and polycapillary optics in particular.

**MXRF with Doubly Curved Crystal Diffraction**

Although x-ray-induced fluorescence has a significantly lower background than electron-induced fluorescence, there is still background arising from scattering of the continuous bremsstrahlung radiation in the sample. This can be reduced by filtering of high-energy bremsstrahlung in polycapillary focusing optics (see Chap. 53) and by use of filters to reduce the low-energy bremsstrahlung as done for...
the spectrum shown in Fig. 5. Recently, efficient collection and focusing of characteristic x rays by Bragg diffraction with doubly bent single crystals has been demonstrated by Chen and Wyttry. The arrangement for this is shown in Fig. 7.

Energy spectra taken with a thin hydrocarbon (acrylic) film with a polycapillary focusing optic, and with doubly curved crystal optics with a mica and with a silicon crystal are shown in Fig. 8. The background reduction for the monoenergetic excitation is evident. Various order reflections are observed with the mica crystal. The angle subtended by the mica crystal is approximately $20^\circ \times 5^\circ$, giving an x-ray intensity only about a factor of three lower than that obtained with the polycapillary lens.

The use of DCCs (doubly curved crystals) in commercial instrumentation has met with commercial success in specific elemental applications. A dual DCC instrument where a DCC is used on the excitation side to create a monochromatic beam for excitation and another DCC on the detection side to limit the region of interest of x-ray fluorescence impinging on the detector provides a highly sensitive and selective detection of sulfur in petroleum streams. Several different embodiments include benchtop, online, and handportable instruments. It is apparent that continued development of DCC-based applications will continue to increase.
FIGURE 6  MXRF images of various elements in a geological sample that contains small volcanic glass inclusions (tens of micrometers in dimension) within a quartz phenocryst. The last two images are the Compton (energy-shifted) and Rayleigh (elastic) scattering intensity maps. (From Ref. 25.)

FIGURE 7  Doubly curved crystal MMEDXRF setup. (Courtesy of XOS Inc. From Ref. 31.)
As discussed earlier, EDMXRF utilizing cooled semiconductor junction detectors is widely used in science and industry. The energy resolution of semiconductor detectors is typically 140 to 160 eV. During the past few years, very high resolution x-ray detectors based on superconducting transition-edge sensor (TES) microcalorimeters, semiconductor thermistor microcalorimeters, and superconducting tunnel junctions have been developed. Although these detectors are still under active development, there have been demonstrated dramatic benefits for MXRF applications.

TES microcalorimeter detectors have the best reported energy resolution (~2 eV at 1.5 keV). A schematic representation of a TES microcalorimeter detector is shown in Fig. 9 and energy spectra for a titanium nitride thin film is shown in Fig. 10 and for a tungsten silicide thin film is shown in

**Ultrahigh Resolution EDMXRF**

**FIGURE 8** Energy spectrum obtained from a thin acrylic sample, measured with a mica doubly bent crystal, a silicon doubly bent crystal, and a polycapillary focusing optic. (From Ref. 31.)

**FIGURE 9** A schematic representation of a TES microcalorimeter detector. The operating temperature is ~50 mK. (From Ref. 32.)
Because the absorbing element on microcalorimeter detectors must have a low thermal capacitance to achieve high resolution and short recovery time (for higher counting rates), and cannot operate closer than 5 mm to the sample (because of thermal and optical shielding), the sensitivity is low. However, by using a collecting and focusing optic between the sample and the detector, the effective area can be greatly increased.\textsuperscript{38} A schematic of such an arrangement with a polycapillary focusing optic is shown in Fig. 12. With such a system, the effective area can be increased to approximately 7 mm\textsuperscript{2}, comparable with the area of high-resolution semiconductor detectors.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{SiN_spectrum}
\caption{Energy spectrum for a TiN thin film on silicon. (From Ref. 37.)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{WSi2_spectrum}
\caption{Energy spectrum for a WSi\textsubscript{2} film on SiO\textsubscript{2}. (From Ref. 32.)}
\end{figure}

Fig. 11.\textsuperscript{32} In each case, the spectrum in the same energy region from a silicon junction detector is also shown for comparison.
Figure 13 shows a logarithmic plot of the energy spectrum for an aluminum-gallium-arsenide sample. This shows the bremsstrahlung background that is present when electrons (in this case, 5 keV) are used as the exciting beam. It is clear that x-ray excitation (especially with monochromatic x rays) will be important in order to use such detectors to observe the low-intensity fine structure to get microstructure and microchemical information with high-resolution energy-dispersive detectors.

**FIGURE 12** Schematic representation of focusing optic for microcalorimeter detector. (From Ref. 38.)

**FIGURE 13** Energy spectrum from aluminum-gallium-arsenide sample measured with a TES microcalorimeter spectrometer. (From Ref. 32.)
29.4 REFERENCES


