

X-ray Crystal Spectrometers and Monochromators in Microanalysis

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Abstract: Castaing's successful implementation and application of the electron probe microanalyzer in 1950 stimulated a flurry of development activity around the world. The later versions of this instrument represented a truly international effort, with significant contributions by scientists from Europe, Asia, and North America. If the probe-forming system of the instrument was its heart, the X-ray wavelength spectrometer was its soul. This article reviews some of the history of spectrometer developments—through the “golden years” of microprobe development, namely the dozen or so years following the publication of Castaing's thesis, to the present. The basic physics of spectrometer and crystal design is reviewed. Early experimental devices, such as those developed by Castaing, Borovskii, Wittry, Duncumb, and Ogilvie are reported. Examples of commercial spectrometers such as those by ARL, MAC, Microspec, and Peak are described. Recent developments such as the combination of grazing-incidence optics with flat crystal spectrometers are noted, and the properties and uses of doubly curved crystals are discussed. Finally, the continued development of doubly curved crystal configurations, such as the “Wittry geometry” for scanning monochromators, and point-to-point focusing diffractors for producing small monochromatic X-ray probes to provide improved detection limits for microanalysis are considered.

Key words: electron probe microanalysis, X-ray spectrometers, X-ray fluorescence, X-ray optics, curved crystals, crystal rocking curve, Johann and Johansson crystals, monochromatic microprobe

INTRODUCTION

Wavelength dispersive (WD) spectrometers are designed so that the diffracting crystal can be positioned at a precise and known angle relative to the incident X-ray beam. Then, if diffraction occurs from a given set of atomic planes, the wavelength is determined by Bragg's law, namely:

$$n\lambda = 2d\sin\theta_B \quad (1)$$

where n is an integer (the order of diffraction), λ is the wavelength of the x-rays, d is the interplanar spacing of the diffracting planes, and θ_B is the Bragg angle measured from the diffracting planes. In this process, the incidence angle, θ_i , need not be precisely equal to the Bragg angle but must lie within a range of values given by the rocking curve width, w , which is a property of the crystal. This condition may be expressed as follows:

$$|\theta_i - \theta_B| \leq w/2. \quad (2)$$

For a given angle of incidence, θ_i , the diffracted beam will

make an angle, θ_r , with respect to the diffracting planes such that $\theta_r = \theta_i$. In addition, under certain conditions, the diffracted beam may have a spread of values, i.e.,

$$|\theta_r - \theta_i| \approx w/2. \quad (3)$$

This spread of the diffracted beam invariably occurs for mosaic crystals when the incident X-rays strike the crystal at various angles, as is true when the X-ray source is small and the crystal is large.

The rocking curve width of crystals ranges from about $5 \cdot 10^{-5}$ radian for a good crystal such as quartz to about $5 \cdot 10^{-4}$ radian for a somewhat imperfect crystal such as lithium fluoride (Birks, 1971c; Alexandropoulos, 1974). The rocking curve width of the crystal will influence both the resolving power of the spectrometer and the effective area of the crystal that, in turn, influences the overall efficiency of the WD spectrometer.

When the X-ray source is very small and the rays are diverging from this source, as is the case for the electron probe microanalyzer, it can be seen that the effective area for diffraction from a flat crystal will be extremely small. On the other hand, a cylindrically curved crystal will have a larger effective area for X-rays incident on its concave surface because the angle of incidence of the X-rays can be close to the Bragg angle over a larger part of this surface. Furthermore, the curved crystal can result in focusing of the incident rays in a manner similar to that of a curved grating for light rays. In analogy to the light case, the curved crystal will have a "focal circle" such that if the source and crystal both lie on this circle, a focus will exist at another point on the circle. The focal circle is sometimes called the Rowland circle as in the light optical case. X-ray spectrometers based on curved crystals are called focusing spectrometers.

The radius of the focal circle is equal to half the radius of curvature of the crystal, as shown in Figure 1a. However, the constraints of Eqs. (2) and (3) result in a significant difference for X-rays compared with light—even for polychromatic radiation only a single diffracted ray is produced. In order to detect X-rays of various wavelengths, the crystal (and often the detector also) must be moved in such a way as to satisfy Eq. (1) for all X-rays to be detected. The only exceptions to this are so-called parallel detection spectrometers wherein a large crystal is used and different parts of the crystal or different planes diffract radiation of different wavelengths. Parallel detection X-ray spectrometers (to be discussed in another section) have not had wide acceptance in electron microprobe instruments. Thus, virtually all

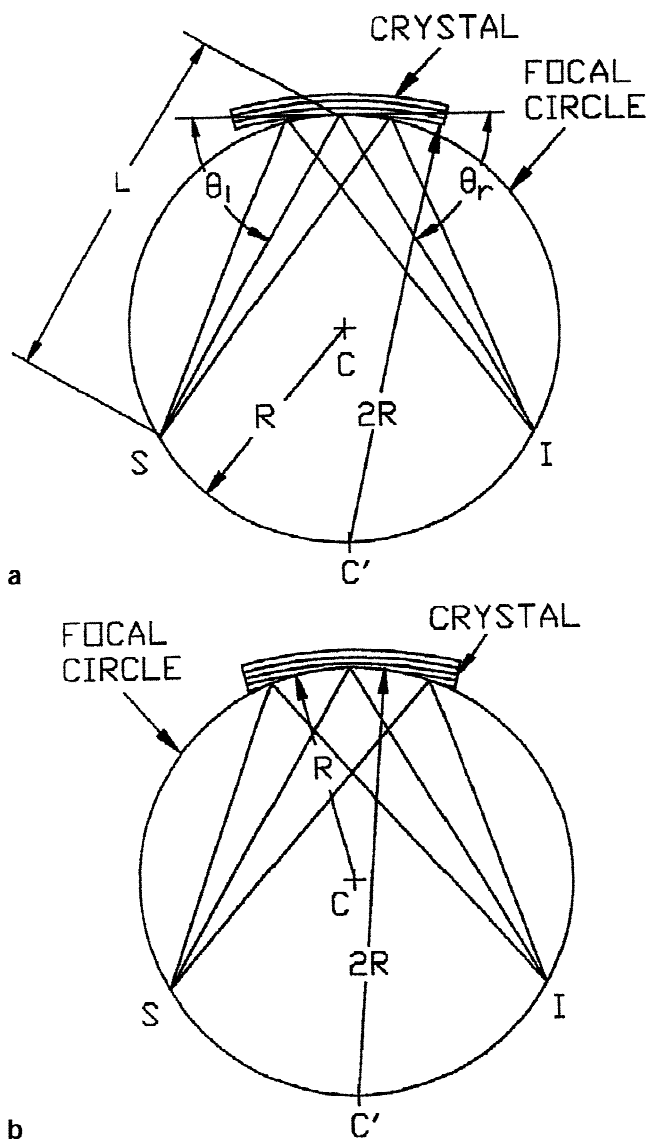


Figure 1. Geometry of focusing spectrometers: (a) Johann; (b) Johansson. Rays diverging from a source S are focused at image I. R and C are the radius and center of the focal circle, respectively. C' is the center of curvature of the crystal planes. θ_i and θ_r are the incidence and reflection angles.

X-ray spectrometers used in microanalysis are actually scanning monochromators.

JOHANN AND JOHANSSON SPECTROMETERS

A Johann spectrometer (Johann, 1931) is obtained by cylindrically curving the crystal to achieve the focusing described in the introduction. The cylindrically curved crystal is called a Johann crystal. The geometry of the rays shown in Figure 1a yields the following equation relating the distance, L, from source to crystal, and crystal to the focal point:

$$L = 2R\sin\theta_B \quad (4)$$

where R is the radius of the focal circle and θ_B is the Bragg angle.

It is important to note that Eq. (2) can only be satisfied for a Johann crystal near the center of the crystal, where it is tangent to the focal circle. Dumond was the first to recognize that it would be possible to satisfy both Eqs. (1) and (2) over the entire surface of the crystal in the plane of the focal circle if the atomic reflecting planes were not everywhere parallel to the surface of the crystal (Dumond, 1955). He proposed a geometry to achieve this in 1930 (Dumond and Kirkpatrick, 1930). The first practical implementation of such a geometry that is shown in Figure 1b was not reported until 1933 (Johansson, 1933). This geometry involves a crystal bent to a radius of $2R$ with its inner surface having a radius of R , where R is the radius of the focal circle. It can be achieved by first bending the crystal to a radius of $2R$ and then grinding its surface to a radius of R , or by starting with a thin lamella that has been ground to a radius of $2R$ and then bending it to a radius of R . The latter procedure was the one used by Castaing for the instrument described in his thesis (Castaing, 1951; Duwez and Wittry, 1955). In addition, Castaing's Johansson crystal was made with the planes offset from being parallel to the focal circle at the tangent point by about 3 degrees. This asymmetry was used advantageously by making the distance from source to crystal larger than the distance from crystal to detector.

Considering the three dimensional aspects of the focus geometries shows that for a point source of monochromatic X-rays, the diffracting region for the Johann geometry is shaped like an X, as shown in Figure 2a (Ditsman, 1960; Wittry and Sun, 1990a). This results because rays that diverge from the plane of the focal circle can satisfy the Bragg angle at points away from the center of the crystal. On the other hand, for the Johansson geometry the diffracting region is a band parallel to the focal circle as shown in Figure 2b (Wittry and Sun, 1990a). Thus, the Johansson crystal will produce a straight line focus while the Johann crystal will produce a focus that consists of two superposed slightly curved lines (Wittry and Sun, 1990b). In Figure 2, the rocking curve width is assumed to be equal to $2 \cdot 10^{-4}$ radians. Wider regions would be obtained for a larger rocking curve width and, conversely, smaller regions would be obtained for a smaller rocking curve width.

The shape of the diffracting regions for Johann and Johansson crystals influences the shape of the crystals used

in practice. Johann crystals might typically have a length to height (width) ratio of about 1.5, whereas Johansson crystals might have a length to height (width) ratio of as much as 3 or more. On the other hand, when several spectrometers are used in the same instrument, the Johann and Johansson crystals are often made the same shape for convenience. Comparison of the relative areas of the diffracting regions in Figure 2 indicates that Johansson crystals should theoretically give greater intensities than Johann crystals by at least a factor of 2 or 3 (depending on the size and shape of the respective crystals). However, the improvements of the Johansson spectrometers over the Johann spectrometers are sometimes less than expected from theory, due to the additional errors of fabrication. In addition, some crystals cannot be ground to the desired Johansson geometry (e.g., mica and layered synthetic microstructures).

The difference in size and shape of the diffracting region will also result in a difference in the best values for the height and width of a slit placed at the focus to eliminate background from scattered radiation. An optimal slit for the Johann spectrometer will be about twice the crystal height. However, both the height and width of the theoretically optimum slit for a Johansson spectrometer will be smaller than the optimum slit for a Johann spectrometer (Wittry and Sun, 1990b). Thus, in addition to giving higher intensity, the Johansson spectrometer will also provide higher signal-to-background ratio if the crystal is well made.

Another type of curved crystal spectrometer should be mentioned in passing. This utilizes a very thin crystal utilized in transmission rather than reflection (Cauchois, 1934). Such spectrometers are not commonly used in electron probe microanalysis for a variety of reasons (refer to the section on Borovskii's microanalyzer).

PARALLEL DETECTION SPECTROMETERS

Before going on to describe some typical focusing spectrometers used in electron probe microanalysis (EPMA), it is useful to indicate some of the approaches to X-ray spectrometry that have been used or proposed to avoid moving the crystal and detector. A summary of some of the approaches is indicated in Figure 3. Further details, as well as references to the various geometries shown in this figure have been given in an article by Wittry and Li (1993). In these cases, a large crystal is used such that different parts of the crystal can diffract radiation of different wavelength. A position-sensitive X-ray detector records the diffracted X-

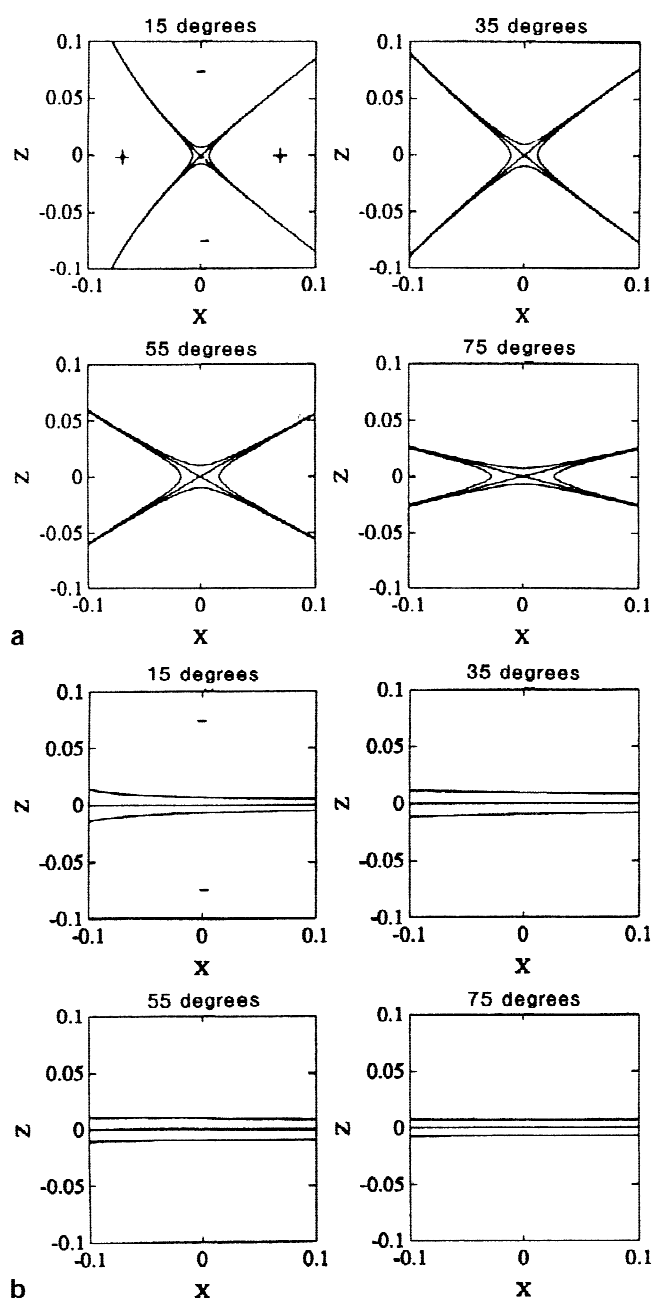


Figure 2. Effective area within which the angle of incidence lies within the rocking curve for $w = 2 \cdot 10^{-4}$ radian for Bragg angles of 15, 35, 55, and 75 degrees. (a) Johann crystal; (b) Johansson crystal. The X and Z values are dimensionless coordinates which are the actual values divided by the focal circle radius. (Adapted from Wittry and Sun, 1990a.)

rays. The first position-sensitive detector to be used was a photographic film.

Interest in parallel detection X-ray spectrometers has been enhanced with the availability of inexpensive charge-coupled device (CCD) arrays that can be used for the

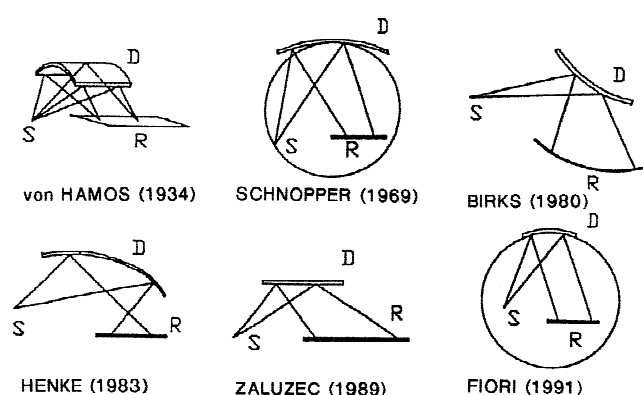


Figure 3. Some parallel detection X-ray spectrometers. In these spectrometers, S is an X-ray source, D is a diffractor, and R is a recording medium (e.g., photographic film or charge-coupled device [CCD] array) (Adapted from Wittry and Li, 1993).

position-sensitive detector. However, practical difficulties and the small number of crystal materials that can be properly configured have limited the use of parallel detection spectrometers to specialized applications where it is essential to have simultaneous recording, or when it is necessary to avoid moving parts such as studies of transient phenomena in plasmas or X-ray astronomy.

Unfortunately, the geometries included in Figure 3 have low efficiency when used for detection of characteristic X-ray lines. This is because these spectrometers have limited collection solid angle for each of the wavelengths detected. Since X-ray characteristic lines are relatively narrow and widely spaced, this means that much of the available collection solid angle is wasted on background radiation. As a result, none of these spectrometers is able to provide performance in microanalysis applications that is competitive with a computer controlled scanning monochromator with its capability of slewing rapidly between characteristic lines of interest (Wittry and Li, 1993).

EXAMPLES OF SPECTROMETERS FOR ELECTRON PROBE MICROANALYSIS

Castaing's Spectrometer

Figure 4 shows a photograph of Castaing's spectrometer (Castaing, 1951). In this design, a curved and ground quartz crystal moved along a circular track that is concentric with the Rowland circle. The crystal was mounted on a holder at the end of an arm attached to a crystal carrier, and a Geiger counter, used as the X-ray detector, was mounted on a fixture at the end of another arm. A quartz crystal and the

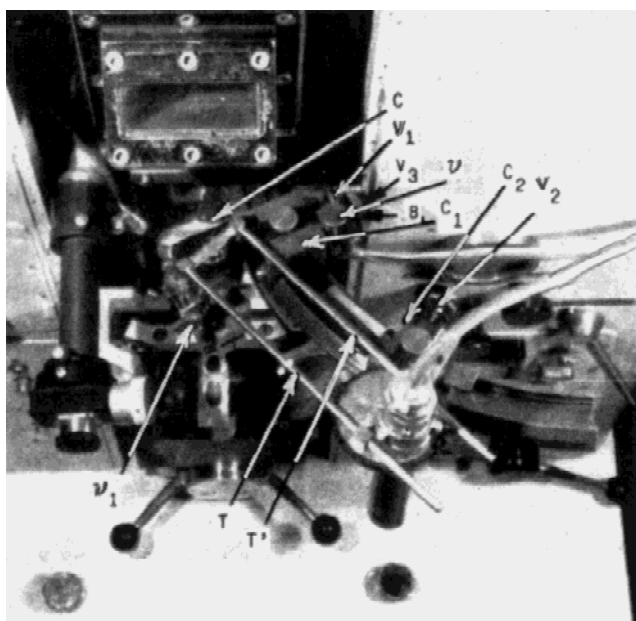


Figure 4. Castaing's spectrometer used with his electron microprobe. The components designated are as follows: C is the quartz crystal holder; C_1 and C_2 are the crystal and detector carriages that move on a common set of ways; V_1 and V_2 are extensible arms for the crystal carriage and detector carriage with lengths adjustable by v_1 and v_2 ; v_3 is an adjustment of the position of the center of the focal circle; B is a knob that turns a shaft passing through the crystal carriage and attached to a gear lying between a stationary rack and a moveable rack which is attached to the detector carriage—when the knob is turned, the detector carriage moves twice as far as the crystal carriage; T and T' are rods that guide the Geiger counter detector; v_3 adjusts the position of the focal circle; additional adjustments are v which moves the carriages relative to each other and v_1 which rotates the crystal about a vertical axis (adapted from Castaing, 1951, with permission).

(10 $\bar{1}1$) planes were used, and the focal circle radius was 250 mm.

Figure 5 shows the configuration of the spectrometer in the context of the entire instrument. The take-off angle was quite low, actually 16 degrees, reflecting the requirement to have a line of sight from the sample to the crystal underneath the large electrostatic objective lens of the instrument. Such a low take-off angle was not as much of a drawback then as it would later become because the soft X-rays from light elements were not detectable due to lack of suitable diffractors. Another implication of the design, in which the crystal moves along an arc corresponding to a part of the Rowland circle, is that the take-off angle varies with wavelength, complicating the quantitative analysis algorithms.

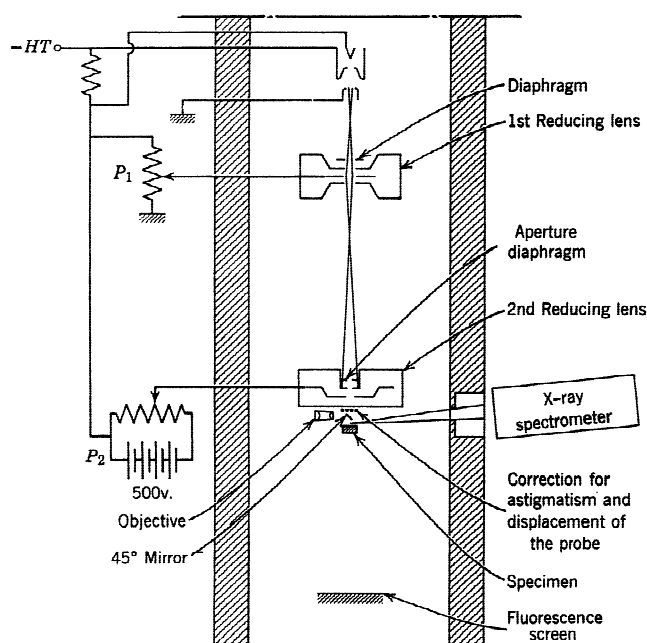


Figure 5. Schematic diagram of Castaing's electron probe micro-analyzer (adapted from Castaing, 1951, with permission). HT is the high voltage for accelerating the electrons; P_1 and P_2 are potentiometers for setting first and second electrostatic lenses.

Borovskii's Spectrometer

Figure 6 shows Borovskii's microprobe and spectrometer which was developed at nearly the same time as Castaing's (Birks, 1971a). Borovskii used a Cauchois-type spectrometer, which detects the diffracted beam transmitted through the crystal. In such transmission spectrometers, the diffracting planes are perpendicular to the surface of the crystal. There were several reasons why others followed Castaing's lead rather than Borovskii's: a) many crystals cannot be made thin enough to be used in the transmission mode; b) the transmitted beam is divergent, precluding the use of a narrow slit at the detector to reduce background; and c) Borovskii's spectrometer moved the source and the detector, keeping the crystal fixed—a configuration that seemed intuitively less practical than keeping the source (which usually includes a large electron beam column) fixed, and moving the crystal which is much smaller.

A later EPMA developed in the USSR that had the designation RSASH-3DS has been described by a colleague of Borovskii (Il'in, 1960). This had two spectrometers: The first was the transmission type for hard X-rays and the second was the reflection type with bellows between the specimen chamber and crystal, and between the crystal and

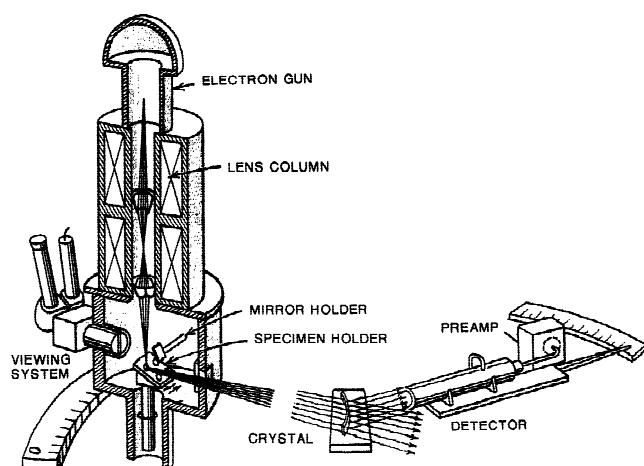


Figure 6. Borovskii's microprobe and spectrometer (adapted from Birks, 1971a).

detector so that the crystal and detector could be operated in the same vacuum as the electron probe. Both spectrometers had the source and detector moving on fixed-center focal circles.

Wittry's Spectrometer

Wittry, in his doctoral thesis (Wittry, 1957), described a microprobe with a spectrometer similar to Castaing's and to many others that were built in research laboratories about the same time (Birks, 1971b). However, his spectrometer was contained inside a cast aluminum housing that could be evacuated. Figure 7 shows the Wittry spectrometer that, like Castaing's, utilized a crystal and detector moving along an arc of the Rowland circle. The detector and crystal arms were mounted on gear sectors that were driven by two pinion gears mounted on a common shaft. This shaft passed through the bottom vacuum wall through a shaft seal and was connected to a large drum on which were scribed the angular positions of various characteristic lines. The shaft containing the pinion gears was driven from below the table containing the spectrometer by a worm gear assembly. The crystals were of the Johansson type, 35×14.3 mm. and used the (10 $\bar{1}$ 1) planes of quartz. The focal circle radius was 265.4 mm.

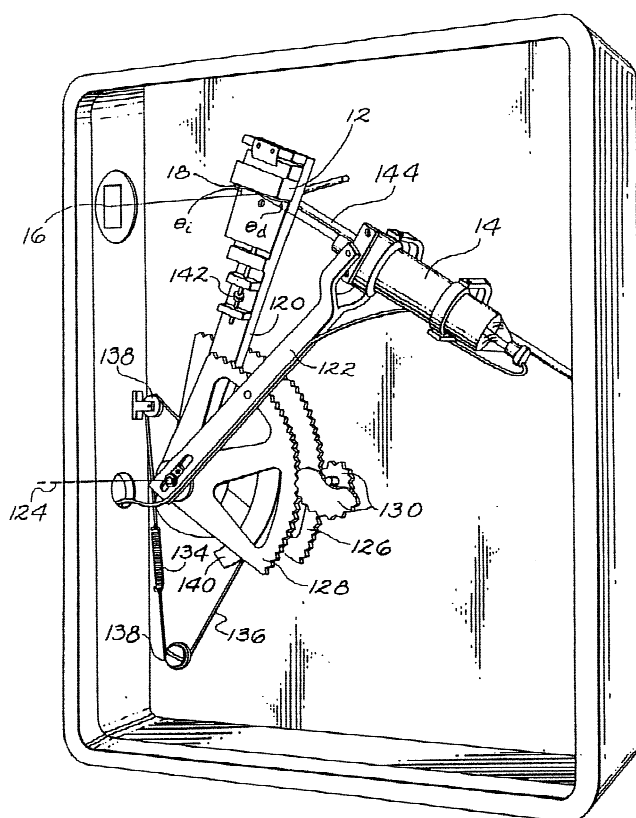


Figure 7. Wittry's spectrometer contained in an aluminum housing that can be evacuated (from Wittry, 1957). The spectrometer supported the electron beam column (not shown). The crystal is 18 and detector is 14. The crystal arm 120 and detector arm 122 are mounted on gear sectors 128 and 126, driven by gears 130 mounted on a common shaft. The gears are selected to provide a 2/1 ratio for detector vs. crystal motion. To prevent backlash, gear sectors 128 and 126 are provided with equal and opposite torque about their common axis 124 by spring 134 and cable 136 that passes over pulleys 138. Rod 144 keeps the detector pointed at the crystal.

the Applied Research Laboratories (ARL) Corporation around 1960, was the prototype of the modern spectrometer. It was based on the design of scanning monochromators that ARL had been using in X-ray fluorescence analysis instruments. Among the unique features that the ARL spectrometers provided are the following:

a) It was one of the first commercial spectrometers developed after Castaing's work in which the spectrometer shared vacuum with the specimen chamber and beam column. Thus, after Henke (1965) developed the use of Langmuir-Blodgett multilayers with 2d values near 100Å in the mid 1960s, analysis of light elements was readily accommodated. Because of the low energy of the X-rays emitted

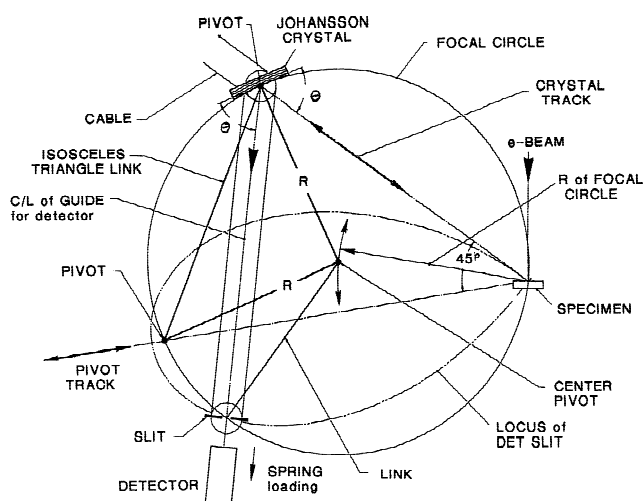


Figure 8. Schematic diagram of Applied Research Laboratories' electron microprobe X-ray (EMX) spectrometer. A cable of constant length maintains the distance from source to crystal equal to the distance from crystal to the detector slit. The crystal moves along one linear track, and a pivot point attached to a second apex of the triangular member formed by the triangle link and arms R moves along a second linear track. These two tracks which intersect at the expected position of the X-ray source generate a circular motion of the third apex of the triangle which is the center of the focal circle. Two adjustments are provided: tilt of the crystal about its center; and motion of the plate on which the spectrometer is mounted about a pivot, at the top of the spectrometer, to align it relative to the X-ray source.

from the light elements, a window between the specimen region and the spectrometer, which would absorb the X-rays, could not be used.

b) The crystal was moved along a straight line as a function of angle, such that Eq. (4) remained satisfied, following the innovation by Sandstrom (1952). Since the distance traveled along the straight line was determined by a leadscrew, the readout was directly proportional to the wavelength. This dictated that the focusing circle rotate about the sample, and that the detector sweep out a complex path, called a lemniscate (Fig. 8). In the EMX, the distance between source and crystal (L_1), and the crystal and detector (L_2), were maintained equal to each other by a system of cables and pulleys while the center of the focal circle traveled along a generated circular path. The added complexity of the detector motion was more than offset by the advantage that the X-ray take-off angle remained constant for all wavelengths, simplifying quantitative analysis. Following the success of the EMX spectrometers, nearly all commercial spectrometers subsequently made for EPMA

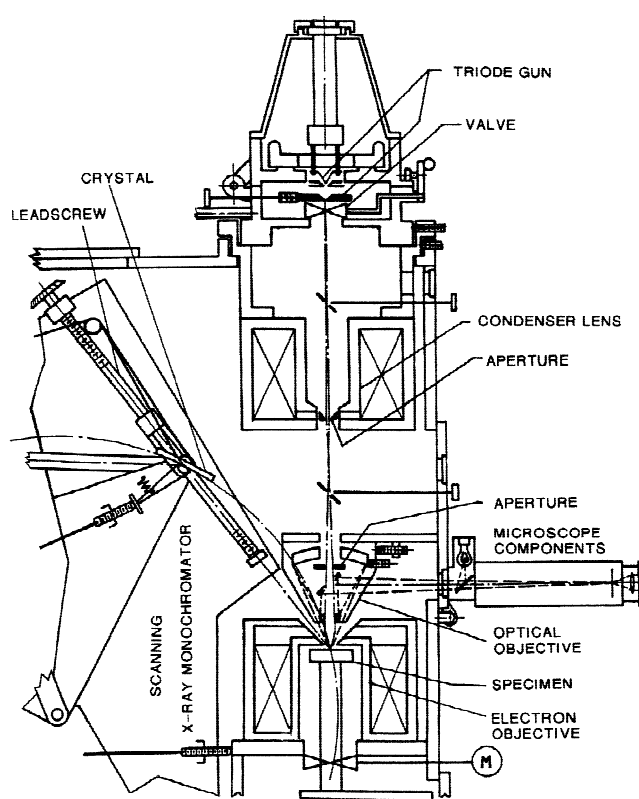


Figure 9. Diagram of Applied Research Laboratories' EMX showing the relationship of the X-ray spectrometer to the optical viewing system and the electron optical column. Motor M drives a gate valve for the specimen airlock.

instruments used a constant take-off angle design. At least one of these, for which a US Patent was assigned to Nehon Denshi (Honme and Komatsubara, 1969), also used a constant-length cable to maintain L_1 equal to L_2 .

c) The EMX used a patented design of the objective lens such that the X-rays were taken back through the lens and the exciting coil was below the lens gap (Wittry, 1959). This "inverted" design allowed an X-ray take-off angle of 52.5 degrees and also provided space for a reflecting objective of high numerical aperture that was coaxial with the electron beam as shown in Figure 9. In later versions, e.g., the electron microprobe X-ray analyzer-scanning microscope (EMX-SM), the large lens coil was replaced with a pancake coil to provide greater space for the specimen.

In the EMX, three spectrometers were mounted inside the vacuum tank. Initially, spectrometers with two different radii of focal circle were available, i.e., 4 inch and 11 inch. The crystals were 1.5×0.5 inches and usually of the Johansson type. As it turned out, the higher resolution of the 11-inch spectrometers was rarely needed and the 4-inch

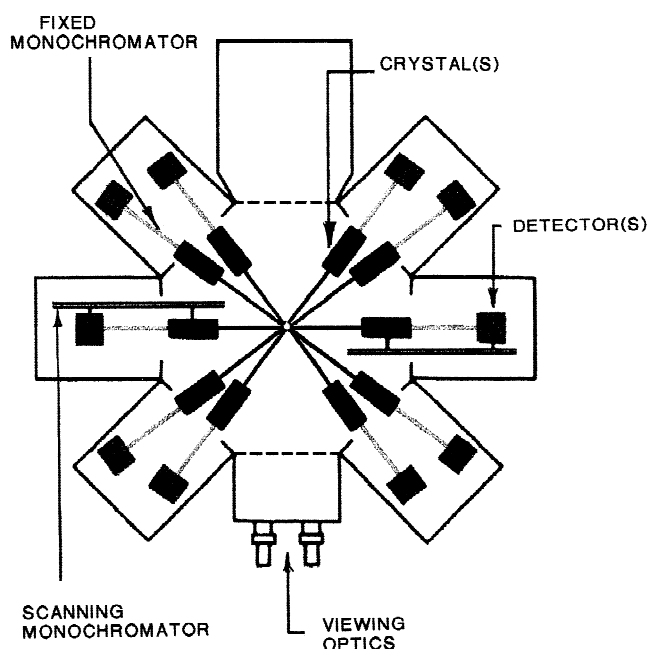


Figure 10. Schematic diagram of Applied Research Laboratories' scanning electron microscope quantometer (SEMQ) showing the typical arrangement for an instrument with 10 monochromators for simultaneous analysis.

radius spectrometers were almost exclusively used because they provided higher intensity. After the initial spectrometer design had been in use for some time, a crystal changer was added. This allowed the use of a second crystal on each spectrometer so that the three spectrometers provided could be used for simultaneous analysis for a wider variety of specimens. In order not to compromise the spectrometer's wide range of Bragg angle (14.5–70 degrees), crystal interchange was done at the high end of the Bragg angle range.

Scanning Electron Microscope Quantometer of ARL

A later model electron probe microanalyzer made by ARL called the scanning electron microscope quantometer (SEMQ) replaced the EMX. It featured an octagonal-shaped beam housing about which six ports were available for X-ray spectrometers (two of the eight sides of the octagon were used for pumping and for the optical viewing system, respectively). On this instrument, the possibility of using fixed X-ray monochromators was introduced, two of which could be located in a single housing fitted for one of the six ports. Thus, as many as 10 spectrometers (two scanning and eight fixed) could be accommodated as shown in Figure 10.

The fixed spectrometers had the crystal and detector

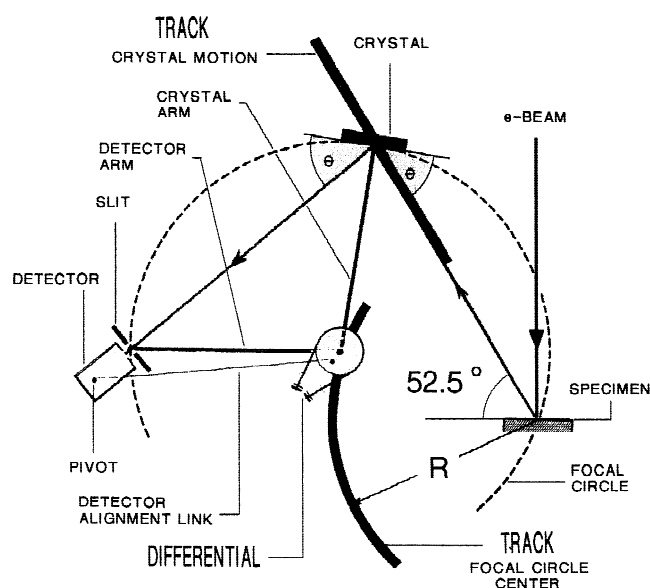


Figure 11. Schematic diagram of Applied Research Laboratories' SEMQ spectrometer. A circular track with radius R (the focal circle radius) constrains the focal circle to rotate about the X-ray source; a linear track having a direction passing through the X-ray source constrains the motion of the crystal. The backlash-free differential maintains $\theta_i = \theta_r$ by means of pulleys and a steel band.

slit prealigned on a fixture. An adjustment for crystal tilt was brought outside of the vacuum housing. Crystals were the same as used in the scanning monochromators. The scanning monochromators utilized a unique backlash-free differential designed by Bela Kennesey to provide a $\theta/2\theta$ relationship. Thus, the cables running between pulleys on the crystal and detector carriages as used in the EMX were no longer necessary. A schematic diagram of the SEMQ spectrometer is shown in Figure 11.

In order to be able to accommodate the additional spectrometers, the radius of the focal circle was increased to 5 inches. Also, to partially compensate for the loss of intensity with the larger focal circle, the crystal size was changed to 1.75×0.5 inches. For Johansson crystals, assuming that the effective area remains within the height, h , of the crystal, the intensity should vary as l/R where l is the length of the crystal and R is the radius of the focal circle. Thus, the ratio of the theoretical intensities for the 5-inch and 4-inch spectrometers would be $(1.75 \times 4)/(1.5 \times 5) = 0.93$. Having additional channels of simultaneous X-ray detection provided more than sufficient advantage to overcome this small loss of X-ray intensity. This instrument proved particularly popular with geologists because of their need to measure many different elements in typical specimens.

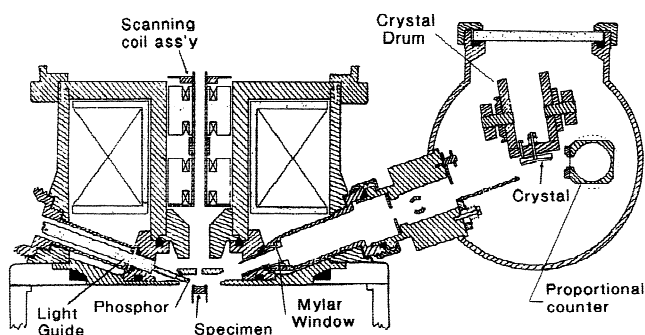


Figure 12. Duncumb's spectrometer for analysis of metal alloys. The crystals were mounted on a turret that rotated about an axis in the plane of the diagram. For scanning, the crystals and detector rotated about an axis perpendicular to the diagram (adapted from Duncumb and Melford, 1960, with permission).

Spectrometers That Deviate from Exact Focusing

If the EMX spectrometer was the ultimate in design features, it was also one of the most complex. Around the same time that the EMX was introduced, Duncumb built a spectrometer, that in contrast, was one of the most simple (Duncumb and Melford, 1960). Duncumb recognized that if it was not necessary to analyze the whole spectrum, a spectrometer could be designed in which the crystal has a fixed position and simply rotates through a limited angular range with the detector located on an arm that rotates about the center of the crystal with twice the angular displacement as the crystal. This is shown in Figure 12. Duncumb's spectrometer was really intended to analyze alloying elements in steel, and utilized a four-crystal turret populated with at least three LiF crystals. A fifth position of the crystal turret allowed the X-ray beam to pass directly into the detector. In this design, L and R in Eq. (4) are both fixed, so that the focusing equation is satisfied only for the one Bragg angle. However, as the crystal is rotated through a small angular range, different parts of the crystal are used and it is still possible to maintain reasonable performance. After that range has been exceeded, another LiF crystal, with a different radius, can be selected by rotation of the turret.

In previous spectrometers, a Rowland circle radius was selected, and the crystal was curved to the diameter of the circle. In Duncumb's spectrometer, however, there were multiple Rowland circles, since each crystal had a unique curvature, depending on the wavelength range over which it was used. A similar spectrometer was described by Hara in a U.S. patent assigned to Hitachi (Hara, 1975). Like Duncumb's spectrometer, the detector rotated about an axis

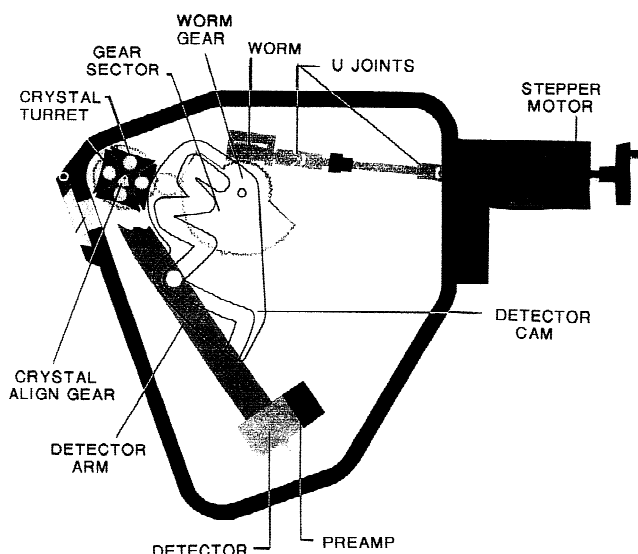


Figure 13. Spectrometer of Peak Instruments (adapted from a Peak Instruments, Inc. brochure, with permission).

through the center of the crystal. However, unlike Duncumb's spectrometer, the axis of the crystal turret was parallel to the axis used for scanning.

This type of spectrometer was reintroduced in 1984 by Peak Instruments and was primarily intended as a light element analyzer to supplement the energy dispersive systems that had become the preferred analysis method on SEMs (but, at that time, were unable to detect light elements due to the Be window on the detector). This spectrometer, called the *Focus*, is shown in Figure 13. It used a stepping motor to drive the crystal through the required range of angles; a shaft, coupled to the crystal by a set of gears, turned a cam that drove the detector through its corresponding range of angles. The track machined in the cam was unique to the set of elements specified for a given spectrometer; it was made by using a computer program that output instructions to a numerically controlled milling machine based on the crystals and wavelengths of interest. Since the crystal change direction was just a continuation of theta, crystal selection, crystal angle, and detector angle were all driven by a single motor, making the spectrometer very compact. A later version, the *IbeX* was modified to use in-vacuum motors to drive the crystal and detector independently, eliminating the need for the cam while retaining the compact size.

The introduction of this spectrometer fortuitously coincided with the introduction of the layered synthetic microstructure (LSM; or multilayer) diffractors that yielded intensities several times higher than the steirates and greatly

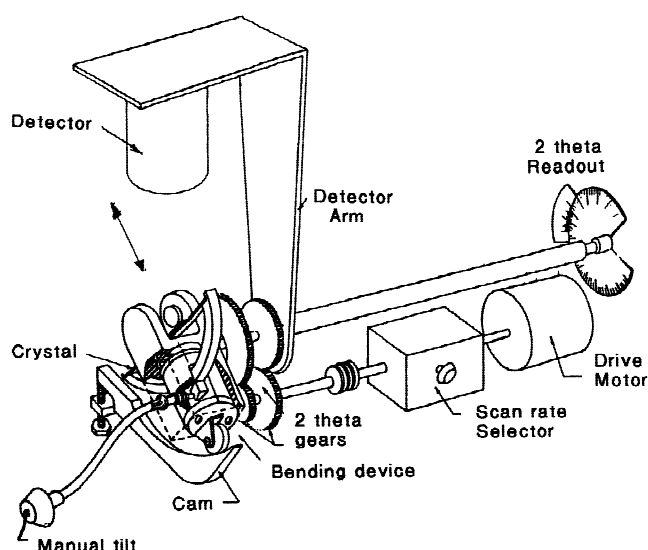


Figure 14. Spectrometer of Elion and Ogilvie. The crystal was bent to different radii in order to scan the spectrum (adapted from Elion and Ogilvie, 1962, with permission).

facilitated, or in some cases enabled, light element analysis (Contardi et al., 1984). These patented multilayers, now produced by Osmic Corporation, were customized for each wavelength, so it was not uncommon to have the turret of the Peak spectrometer populated with three different multilayers ($\text{Mo/B}_4\text{C}$ for boron, Ni/C for C, and W/Si for oxygen and nitrogen).

Spectrometer of Elion and Ogilvie

Also in the early 1960s, Elion and Ogilvie built a spectrometer that, like Duncumb's, eliminated the need to translate the crystal (Elion and Ogilvie, 1962). This spectrometer, however, maintained the focal circle relationships of Eq. (4) continuously through a range of angles by flexing a mica crystal through a range of curvatures as a function of θ_B (Fig. 14). The fact that this type of spectrometer did not proliferate was probably due to the difficulty in making crystals other than mica that could be subjected repeatedly to elastic flexing.

Spectrometer of Materials Analysis Corporation

Although the Materials Analysis Corporation (MAC) 400 spectrometer may not have been particularly noteworthy in itself, the instrument and the company were quite significant in microprobe and spectrometer history. Around 1960, Macres, who studied under Ogilvie at the Massachusetts

Institute of Technology (MIT), and who later built a microprobe at Stanford, started MAC to commercialize his design. The competitive pressure forced on the industry by ARL with its high take-off angle, dictated that new instruments also have a high take-off angle. However, ARL's inverted lens design was patented, so the MAC 400 achieved its 38.5-degree take-off angle by inclining the sample. Many of the leaders in the microprobe community strongly objected to the use of an inclined sample, as all the quantitative algorithms were either developed or substantiated using normal electron beam incidence on the specimen.

Despite the controversy over the ability to perform accurate quantitative analysis with the instrument, the MAC 400 was quite successful. Inclining the sample not only allowed a higher take-off angle, but also allowed space for a high-quality light microscope objective of the transmission type. This was of particular interest to mineralogists who used polarizing light microscopes for the identification of mineral phases.

Spectrometers of Microspec Corporation

R. Wolf and W. Donnelly who had both worked at various times for MAC, identified a need for a WD spectrometer that could be sold as an accessory to the scanning electron microscopes (SEMs) that were becoming increasingly popular in the late 1960s. They incorporated Microspec in 1970, and shortly thereafter introduced the model 210, designed initially under a contract with Cambridge Instruments. This spectrometer included a vacuum housing that was attached to the vacuum housing of the SEM. In order to accommodate various SEMs, the focal circle radius was relatively large, 210 mm, and large crystals were used. In the model 400, that had a four-crystal changer, the crystals were 48 mm \times 20 mm. A later model, the 600, had a six-crystal changer and crystals that were 40 mm \times 15 mm. Crystals of LiF were made in the Johansson geometry, but crystals of pentaerythritol (Pet) and thallium acid phthalate (TAP) were bent and then ground over only two-thirds of the central part of their surface. The most identifying feature of this spectrometer was the use of a horizontal Rowland circle.

The horizontal orientation of the Microspec spectrometers was partly the result of making it adaptable to existing SEMs. But we must note that it had an advantage because of the difficulty of accurately positioning a specimen in the vertical direction in most SEMs. Spectrometers that are oriented more or less horizontally have crystals with the axis of

the cylindrical curvature nearly vertical. For these spectrometers, the location of the specimen in the vertical direction is not as critical as it is for spectrometers with their focal circle in the vertical plane.

SPECTROMETER ORIENTATION AND ITS CONSEQUENCES IN EPMA

Like the SEM with add-on spectrometers, some early EPMA instruments had the focal circle of the spectrometer in the horizontal plane or the inclined plane containing the direction of the X-rays' take-off. Also like the SEM, these cases have minimum sensitivity to vertical specimen displacement. But most modern EPMA instruments have focal circles that lie in the vertical plane in order to be able to accommodate more than two spectrometers. In these instruments, the X-ray intensities are extremely sensitive to specimen position, a circumstance that is not serious because the operator can make use of the small depth of field of the optical viewing system that is usually provided to set the specimen height accurately. For these cases, the X-ray intensities are relatively insensitive to electron probe displacements in one direction, and strongly sensitive to displacements in the direction perpendicular to this. Methods to overcome this problem for making compositional maps include sweeping the beam electronically in the direction of least sensitivity, and moving the specimen mechanically in the other direction or moving the spectrometer setting as the beam scans. Alternatively, the software used for correcting the X-ray intensities to obtain the composition can be used to correct for sensitivity variations. This approach, as well as the ones based on hardware, has been discussed by Newbury and his coworkers in a two-part article (Newbury et al., 1990a, 1990b).

CRYSTAL SPECTROMETERS IN THE TRANSMISSION ELECTRON MICROSCOPE

Much smaller volumes can be analyzed with X-rays produced by an electron probe by using thin sections such as those employed in the transmission electron microscope (TEM). For such specimens, the beam is broadened only slightly by electron scattering. This is in marked contrast to the thick specimen case for which electron scattering is the dominant factor in determining the size of the volume excited. In addition, thin specimens afford the prospect of

simultaneously focusing the transmitted electrons to form images of high resolution.

The first instrument combining transmission electron microscopy with microanalysis (EMMA) using a WD spectrometer was built by Peter Duncumb at Tube Investments Research Laboratories (Duncumb, 1966). A cross-sectional diagram is shown in Figure 15. Duncumb tried to make the crystal come as close as possible to the specimen, thus dictating a small radius focal circle. Then, in order that the spectrometer mechanism be clear of the probe-forming and objective lenses, the mechanical center of the focal circle was displaced outward, and the detector and crystal were brought back onto the true focal circle by arms of appropriate length. Crystals of mica and LiF were interchangeable under vacuum conditions enabling detection of all elements from sodium (at. no. 11) upward.

The EMMA instrument was completely redesigned in collaboration with Associated Electrical Instruments (AEI), and about 20 were sold for the analysis of thin films and particles under the name of EMMA-4. Because of the low intensities available, the practical limit to resolution, using WD spectrometers for analysis, appeared to be about 0.1 μm .

It is interesting to note that others have attacked the problem of interference caused by the use of spectrometers with a small focal circle radius in electron microprobe instruments. Tomura described a spectrometer that also provided for the center of the focal circle to be located in a region occupied by other parts. A patent on this spectrometer was assigned to Hitachi (Tomura, 1969). Another spectrometer that overcame the same problem in a different way was described in a patent assigned to Cameca (Guernet and Boissel, 1975).

Another approach to combining WDS and TEM is to construct miniature crystal spectrometers for use on existing transmission electron microscopes. Lyman and Wittry proposed a project under the Small Business Innovation Research (SBIR) program to do this for a ultrahigh vacuum (UHV) scanning transmission electron microscope being made for Lehigh University. The proposal was approved by the agency for support, but before the funding could be arranged, the U.S. company involved in collaboration on the crystal fabrication was bought by an English company, and the project was no longer eligible for support under the SBIR program.

The problem of extremely low X-ray intensities from thin specimens in the TEM can be overcome if only a single element is to be detected. Then a crystal with double cur-

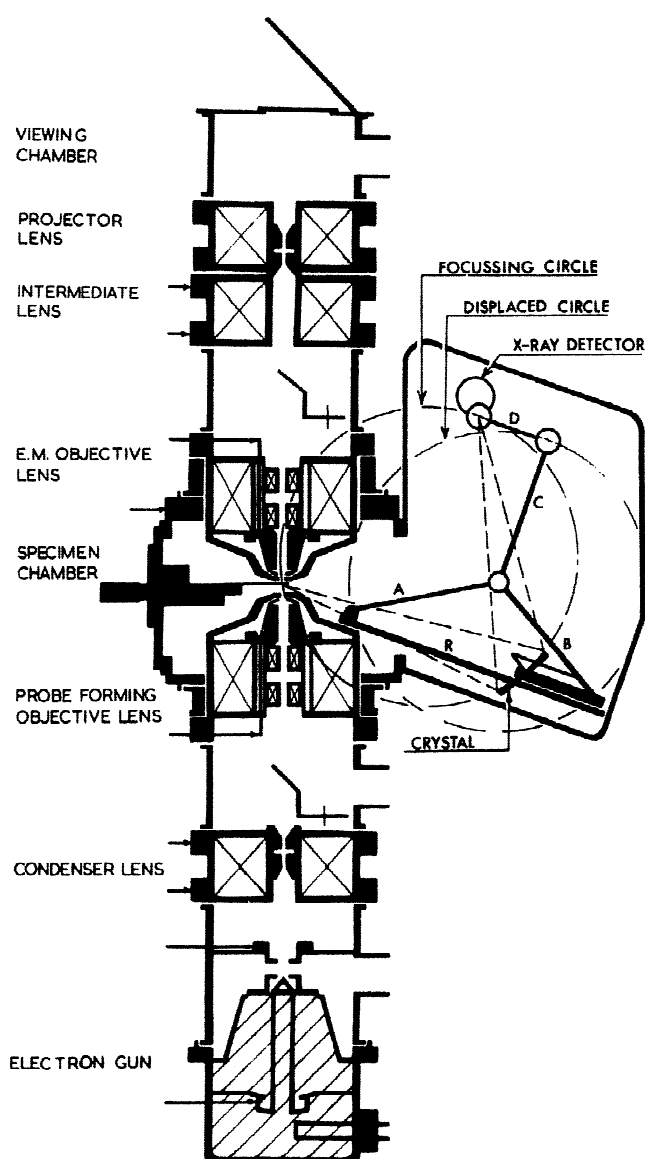


Figure 15. Duncumb's electron microscope microanalyzer (EMMA). (Duncumb, 1966). Note the use of a displaced focal circle to avoid the interference of the circle's center with the column housing. This also allows for a fixed pivot point for the center of the displaced focal circle to move about. Links A, B, and C, which have a length equal to the focal circle radius, define the displaced focal circle. Link D positions the detector back on the true focal circle and a similar link at the end of B positions the crystal back on the true focal circle. The crystal moves linearly along the path R. Reproduced by permission of The Electrochemical Society, Inc.

vature can be used to collect radiation over a larger solid angle than is possible with singly curved crystals. Detection of Ca in the presence of K in biological specimens was the goal of work by Sun, Tormey, and Wittry (Sun et al., 1990),

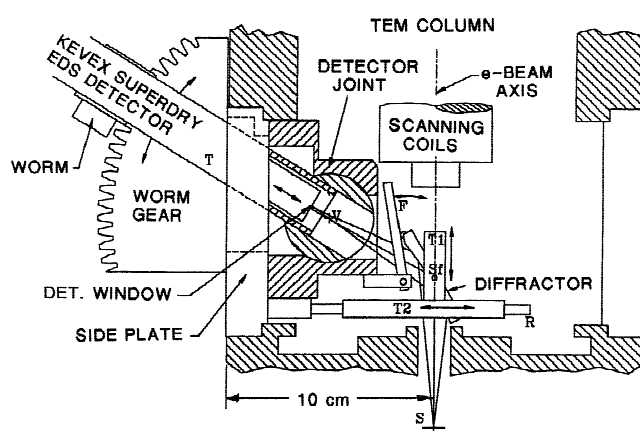


Figure 16. Spectrometer for transmission electron microscope developed by Chen and Wittry (1997b). The diffractor, which has a hole for the passage of the electron beam, translates along T1 parallel to the electron beam which strikes the specimen at point S. While translating, the diffractor is tilted about Sf by adjustable ramp F so that the focal circle passes through the point of intersection of line T1 and ramp F. This intersection point can be made to coincide with S by means of two horizontal translations, for example, T2, which is constrained by rail R. A slit (not shown) can be adjusted to coincide with the virtual crossover of the diffracted rays by translation T and by rotation with the worm gear. This slit reduces background due to scattering and fluorescence.

and subsequently by Chen and Wittry (1997b). Both projects utilized the JEOL 100CX, a transmission electron microscope that had a large space above the objective lens, and ports in the front and sides for access to this space.

The spectrometer of Sun, Tormey, and Chen used a toroidally bent crystal of LiF and a flow proportional counter. The spectrometer received X-rays back through the objective lens (the crystal having a hole for passage of the electron beam). In addition to being able to have a large solid angle, it was thought that the relativistic effect on the angular distribution of the continuum would yield lower background by a factor of two or more compared with detection at right angles to the beam.

This initial attempt was unsuccessful because of poor reflectivity of the LiF (presumed to be due to excess mechanical deformation) and inadequate provisions for alignment. A second spectrometer was made that provided for limited scanning, had the necessary alignment provisions, and could be used with a variety of crystals (Chen and Wittry, 1997b). This spectrometer is shown in Figure 16. The detector utilized was a Peltier-cooled Si(Li) which provided the possibility of studying the origin of stray radiation

due to fluorescence or scatter from the crystal or the instrument walls.

Crystals were made that had a segmented toroidal geometry or a segmented logarithmic spiral geometry (Wittry et al., 1993; Grimm et al., 1995). Unfortunately, only mica was tried as a crystal material because of limited time and funds. Due to mica's low reflectivity, combined with some fabrication errors, the results obtained were only marginally competitive with modern solid-state energy-dispersive spectrometers (EDS). However, with better crystal material, this approach still seems to be capable of providing results substantially better than can be obtained with EDS. Crystal monochromators are particularly important when there are peaks in ED spectra that overlap and the element of interest has low concentration, as is the case for the K_β line of potassium and the K_α line of calcium.

COLLECTION EFFICIENCY OF WD SPECTROMETERS

The ability of WD spectrometers to collect X-rays from a point source is limited by the solid angle subtended at the source by the effective area of the crystal and by the peak reflectivity in the crystal's rocking curve. Even if the peak reflectivity approaches unity as it may for some crystals, the solid angle subtended by the crystal's effective region is usually limited by the crystal's rocking curve width. Referring to Figure 2a, it can be seen that once the crystal size is large enough to contain the part of the pattern near the center and the wider part of the limbs, little is gained by using larger crystals. Thus, for small rocking curve width, the crystal and focal circle size are relatively unimportant for Johann crystals.

For Johansson crystals, as can be seen from Figure 2b, the relative intensity of a WD spectrometer should increase linearly with crystal length, and inversely with the first power of the focal circle radius, if the crystal is always wide enough to contain the characteristic pattern and the rocking curve is unchanged. This is true because the angular divergence for the diffracted rays in one direction is determined by the width of the rocking curve (hence the l/R dependence and not l/R^2). The situation is more complicated for Johann crystals with large rocking curve width because the shape of the effective area changes with Bragg angle. Moreover, the width of the rocking curve is not always a constant; for most crystals, it depends on surface treatment, i.e., etching or abrading. For LiF and other crystals subject to plastic de-

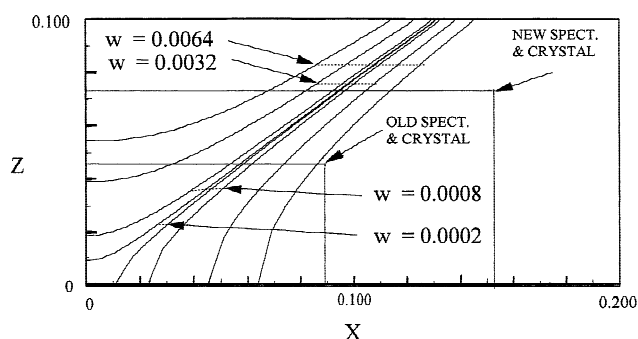


Figure 17. Effective area of one quadrant of a Johann diffractor for a Bragg angle of 35 degrees comparing the size of a small crystal on a 5-inch focal circle spectrometer (old) with a larger crystal on a 4-inch radius focal circle spectrometer (new) for different rocking curve widths w . Assuming a rectangular approximation to the rocking curve, the relative collection efficiency can be estimated by the relative areas contained within the boundaries on each crystal. Note that at $X = 0$, the Z dimension of the effective area of a Johansson crystal is given by the same value as the Johann diffractor.

formation, it may change with bending procedures and radius of bending (Birks and Seal, 1957).

In order to get higher intensities with WD spectrometers, JEOL recently introduced a spectrometer that had a focal circle radius of 100 mm and used crystals 31.5×14.7 mm (instead of the 140 mm radius and crystals 25×12 mm). This represents a good example to explain the theory and to show why it is difficult to get an improvement of intensity by a factor of approximately 3 that would be expected if all the surface of both crystals were used, i.e., an intensity that is proportional to crystal area/ R^2 . We shall not attempt a comparison of theory and experimental results because the experimental results are very sensitive to crystal alignment (Wittry and Chang, 1992) and to the accuracy of crystal fabrication.

First, we must recognize that the effective area scales with the radius of the focal circle (remember that plots like the ones in Fig. 2 are in normalized coordinates—actual coordinates divided by the focal circle radius). Next, let us consider a plot of the effective area relative to the crystal size for the two cases, 140- and 100-mm focal circle, for various values of the rocking curve width. This is shown in Figure 17 for one quadrant of the crystals and a Bragg angle of 35 degrees. We see that even for a rocking curve width of 0.0064 radian or 0.36 degrees, only about 81% of the smaller crystal's surface is effective, and only about 54% of the larger crystal is effective, assuming a rectangular rocking

curve. Note that these percentages refer to the area in dimensionless coordinates, i.e., actual area/ R^2 . Then the relative area of the effective regions indicates an improvement in intensity by a factor of about 2 for this Johann case. For the Johansson case, the relative area also indicates an improvement of about 2.0 times (note that the height of the central region of the Johann crystal is the height of the effective region, i.e., the band for the Johansson crystal). We must remark that Figure 2 and Figure 17 do not take into account the penetration of the X-rays into the crystal (this would make the effective areas slightly larger).

A rocking curve width of 0.36 degrees is somewhat large—for the 4-inch focal circle at 35 degree Bragg angle, slits of about 0.76 mm width are required to contain the focus. To get a feeling for what a rocking curve of 0.36 degrees means, we can calculate the rocking curve width that would cause the Cu $K\alpha$ doublet to wash out. This turns out to be about 0.2 degrees. Thus, a rocking curve width of 0.36 degrees is probably not difficult to obtain by surface treatment. But, we must also remember that large rocking curve widths will adversely affect the spectrometer resolution, and the resulting peak-to-background ratio will be lower. Note that in this result, we see the usual property of spectrometers *of a given design*, whether in the optical or the X-ray region, namely: There is invariably a trade-off between collection efficiency (or transmission) and resolution.

RECENT DEVELOPMENTS

The need for greater collection efficiency of WD spectrometers has prompted two improved spectrometers that combine collimating optics with wavelength dispersive crystals. The first of these, was demonstrated by Barbi and Ohara with the aid of an SBIR supported by the Department of Energy (Barbi, 1996; O'Hara, 1997, 1998). A total reflecting collimating optic in the form of a truncated paraboloid (resembling a tapered tube) was used to collect and transmit X-rays to a spectrometer mounted on a port of an SEM chamber. Since the optic converts a divergent beam into a collimated or nearly parallel beam of X-rays, curved crystals are not necessary and Eq. (4) does not apply. That is, the crystals can remain at a fixed distance from the sample for all wavelengths, and the source-to-crystal distance is not a factor in determining efficiency. The optic used in this case was optimized for light elements, from beryllium to oxygen, and resulted in order-of-magnitude improvements in intensities compared with conventional spectrometer perfor-

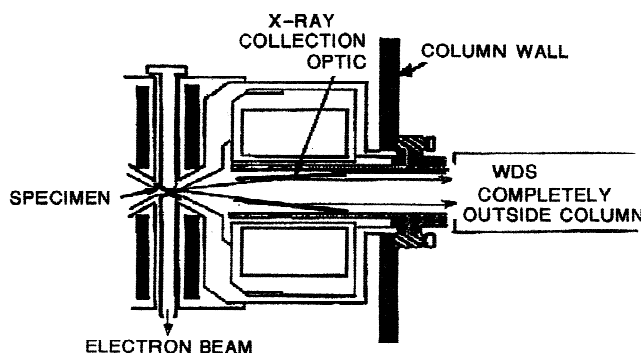


Figure 18. Total reflection collimating optic and flat crystal for use with TEM instruments. WDS, wavelength dispersive spectrometer. (Adapted with permission from Barbi, 1996).

mance. The efficiency of this spectrometer is determined by the distance to the entrance of the optic, the efficiency of the optic, and diffraction efficiency. The efficiency of the optic depends on the critical angle for reflection, and this, as well as the optic size and distance from the source, influence the effective entrance aperture. It was further demonstrated that the optic was of suitable size that it could be placed inside the existing port of at least one commercial TEM. Figure 18 illustrates the configuration of this instrument. The optic is placed inside the port of a side-entry TEM, while the spectrometer resides completely outside the chamber.

Noran Instruments has since devised and patented a hybrid optic that employs a polycapillary optic nested inside the low-energy grazing incidence optic (McCarthy and Howard, 1999). This is suitable for the 0.1–10 keV range. Noran has demonstrated that such a configuration can enable use of a WD spectrometer on cold field emission gun (FEG) SEMs (Rhode et al., 1999) and on large chamber instruments such as defect-review tools (DRTs). Figure 19 illustrates the use of an optic placed close to the source while a flat crystal spectrometer resides quite far away, as it must when adapted to the chamber of a DRT.

Another approach to obtaining a higher collection solid angle with crystal monochromators is to use doubly bent crystals instead of cylindrically curved ones. Early work involving doubly curved crystals was summarized in an article by Golijanin and Wittry (1988). The general case of a diffractor with planes curved to two different radii of curvature, parallel and perpendicular to the focal circle, and surface curved to two other radii of curvature was treated theoretically by Wittry and Sun (1992). The most efficient crystal geometry for detection of a single element is a point-

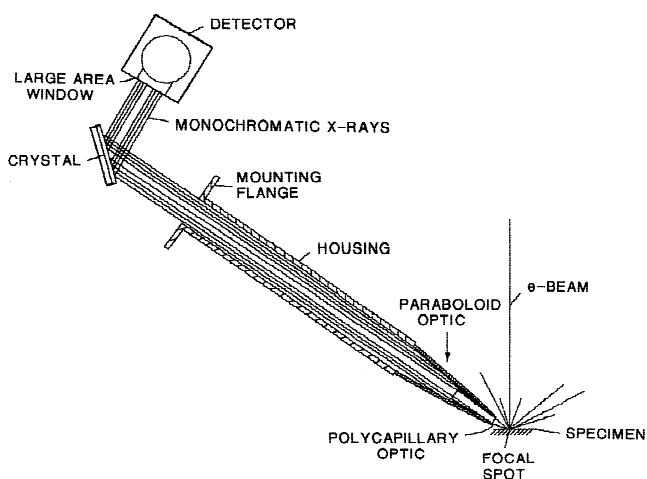


Figure 19. Noran's hybrid collimating optic and flat crystal (adapted with permission from McCarthy and Howard, 1999).

to-point focusing geometry obtained by rotating the Johansson geometry about a line joining the source and image (Golijanin and Wittry, 1988). This is shown in Figure 20. The radius of curvature R_2 of the planes and of the surface perpendicular to the focal circle is given by the following equation:

$$R_2 = 2R_1 \sin^2 \theta_B \quad (5)$$

where R_1 is the radius of curvature of the crystal's surface in the plane of the focal circle, i.e., the focal circle radius, and θ_B is the Bragg angle. The implications of Eq. (5) are that the second curvature is always sharper than the first (for small θ_B , R_2 is very small, making crystal fabrication difficult) and maximum collection efficiency occurs only at one Bragg angle.

The most efficient geometry for use over a wide range of Bragg angles is one with spherically curved planes having a radius $2R$, and a toroidally curved surface with radii R in the plane of the focal circle and $2R$ perpendicular to it. It is like the point-to-point diffractor for θ_B equal to 90 degrees. The effective area for this configuration, called the Wittry geometry, is shown in Figure 21 (Wittry, 1989; Wittry and Sun, 1990a). Comparison of this figure with Figure 2b shows that a crystal of this geometry can provide much larger collection efficiency—a factor that can be 3 to 7 or 8 times that for the Johann crystal (the improvement is greater for small rocking curve width). Moreover the peak-to-background ratio can still remain high—unlike the case of trying to get larger collection efficiency with Johann or

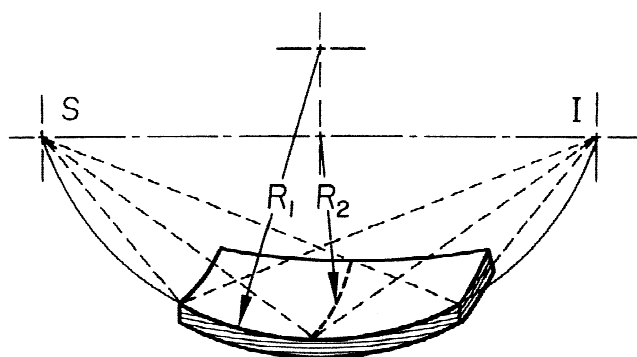


Figure 20. Point-to-point focusing geometry based on rotating the Johansson geometry about a line joining the source S and image I (from Wittry and Golijanin, 1988). A similar point focusing geometry can be obtained by rotating the Johann geometry about a line through S and I, but the collection efficiency will be lower.

Johansson crystals by just trying to make the rocking curve width greater.

FUTURE DEVELOPMENTS

Singly curved crystals will remain the most common for conventional WD spectrometers for electron beam instruments because they are versatile and easy to manufacture. Increased collection efficiency of spectrometers with diffractors of the Wittry geometry are expected to be important in instruments intended for trace analysis because of higher collection efficiency and higher peak-to-background ratio.

The increased efficiency of WD spectrometers, when used in conjunction with X-ray collimating optics, will allow the use of WD spectrometers on large chamber instruments such as defect review tools used in semiconductor process control, FE SEMs, and perhaps even TEMs. An added benefit of a parallel beam spectrometer is that flat crystals are dictated.

Point-to-point focusing crystal diffractors are expected to find use as specific element analyzers in instruments dedicated to specific research problems. They are also particularly well-suited for use in forming monochromatic X-ray microprobes. Chen and Wittry have demonstrated that when doubly curved crystals are used in conjunction with a micro-focus X-ray tube, an intense, highly monochromatic beam can be produced in a small spot (Chen and Wittry, 1997a, 1998). An instrument incorporating this technique, called monochromatic microprobe X-ray fluorescence

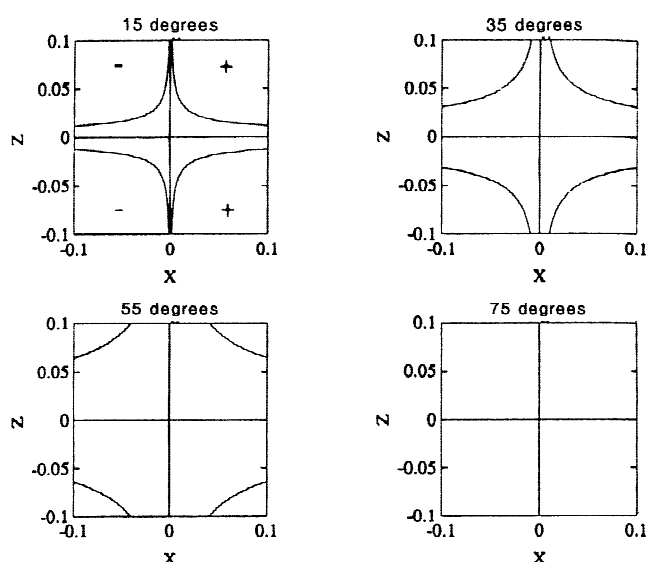


Figure 21. Effective area of the Wittry geometry for which the angle of incidence lies within the rocking curve for $w = 2 \cdot 10^{-4}$ radian for Bragg angles of 15, 35, 55, and 75 degrees. Comparison with Figure 2 shows that the area is much larger for the Wittry geometry than either the Johann or the Johansson geometry. As in Figure 2b, X and Z are the actual coordinates divided by the focal circle radius (adapted from Wittry and Sun, 1990a).

(MMXRF), will have significant sensitivity advantages over electron beam instruments because of the absence of continuum background, and would require simpler algorithms for standardless quantitation because of the monochromatic incident beam.

Other advantages over excitation by electron microprobes include the lack of specimen charging, ease of specimen preparation, possibility of examining specimens in air, and minimum damage of sensitive specimens. Figure 22 illustrates the components of an MMXRF instrument. Using mica, a spot of about 50 μm diameter has been obtained. Use of a quartz crystal, with its smaller rocking curve width, is expected to yield X-ray focal spot sizes 10 μm or less in diameter. In fact, Forster et al. (1991) have already demonstrated that it is possible, using a toroidally bent quartz crystal with similar radii of curvature, to obtain a spatial resolution of 10 μm in an X-ray microscope. Moreover, detection limits in the ppm range should be possible for a 1-min measurement time using recently developed silicon drift detectors which are used as an EDS capable of much higher counting rates than Si(Li) detectors and can be used at near room temperature (Struder et al., 1999). In addition, high-sensitivity detection of elements throughout the periodic table can be done with the use of multiple

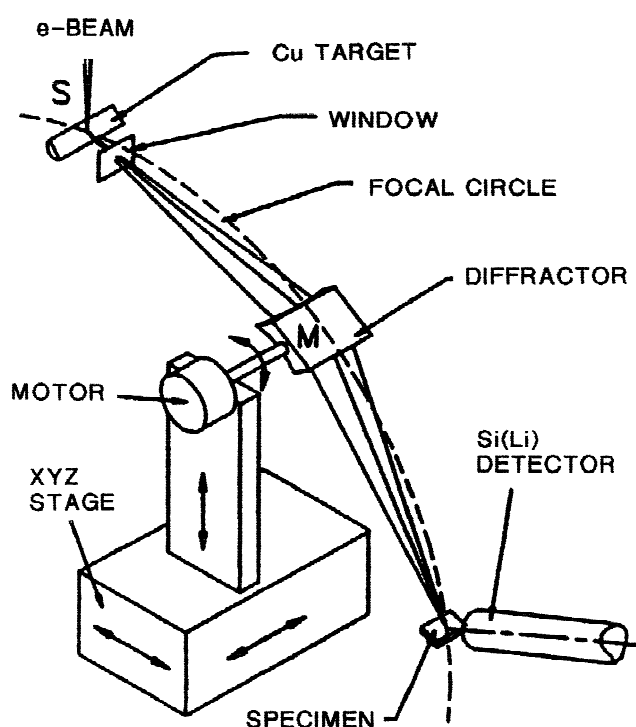


Figure 22. Schematic diagram of the arrangement for demonstrating monochromatic microprobe X-ray fluorescence (MMXRF) (adapted from Chen and Wittry, 1997a). The point-focusing diffractor focuses monochromatic radiation from a microfocus X-ray source S to a small spot on the specimen. Alignment of the diffractor is done by x-y-z translations and rotation about axis M passing through the midpoint of the diffractor's surface.

X-ray diffractors and sources as described in a recent U.S. patent (Wittry, 1999).

With all these prospects for future instruments coming about, perhaps there will be some return to the enthusiasm and activity that followed the development of the first EPMA instrument by Castaing 50 years ago.

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