Variations in the number of protons between elements cause differences in the energy levels of each electron shell. As a result, the energy differences between shells (and therefore x-ray energies) of one atom differ from those of another atom. This is illustrated by the spectra of nickel (Z = 28) and copper (Z = 29).

X-ray	Energy (KeV)	X-ray	Energy (KeV)
$Ni_{K_{\alpha_1}}$	7.477	$Cu_{K_{\alpha_1}}$	8.047
$Ni_{K_{\alpha_2}}$	7.460	$Cu_{K_{\alpha_2}}$	8.027
$Ni_{K_{\beta_1}}$	8.264	$Cu_{K_{\beta_1}}$	8.904
$Ni_{K_{\beta_2}}$	8.328	$Cu_{K_{\beta_2}}$	8.976
Ni_{L_α}	0.849	Cu_{L_α}	0.928
Ni_{L_β}	0.866	Cu_{L_β}	0.948

In addition to the characteristic energy, each electron has a characteristic wavelength. Energy and wavelength are related through the following equations:

1. $$E = h\nu$$
2. $$\nu = c/\lambda$$

where: E = the energy of an x-ray
λ = the x-ray's wavelength
ν = the x-ray's wave frequency
c = the speed of light $\approx 3.0 \times 10^8$ m/sec
h = Planck's constant $= 6.6262 \times 10^{-34}$ joules $\times$ sec

Combining equations 1 and 2, and substituting the values given for h and c, the relationship between energy (in KeV) and wavelength (in Angstroms) is expressed as:

3. $$\lambda = \frac{hc}{E} = \frac{12.396}{E}$$

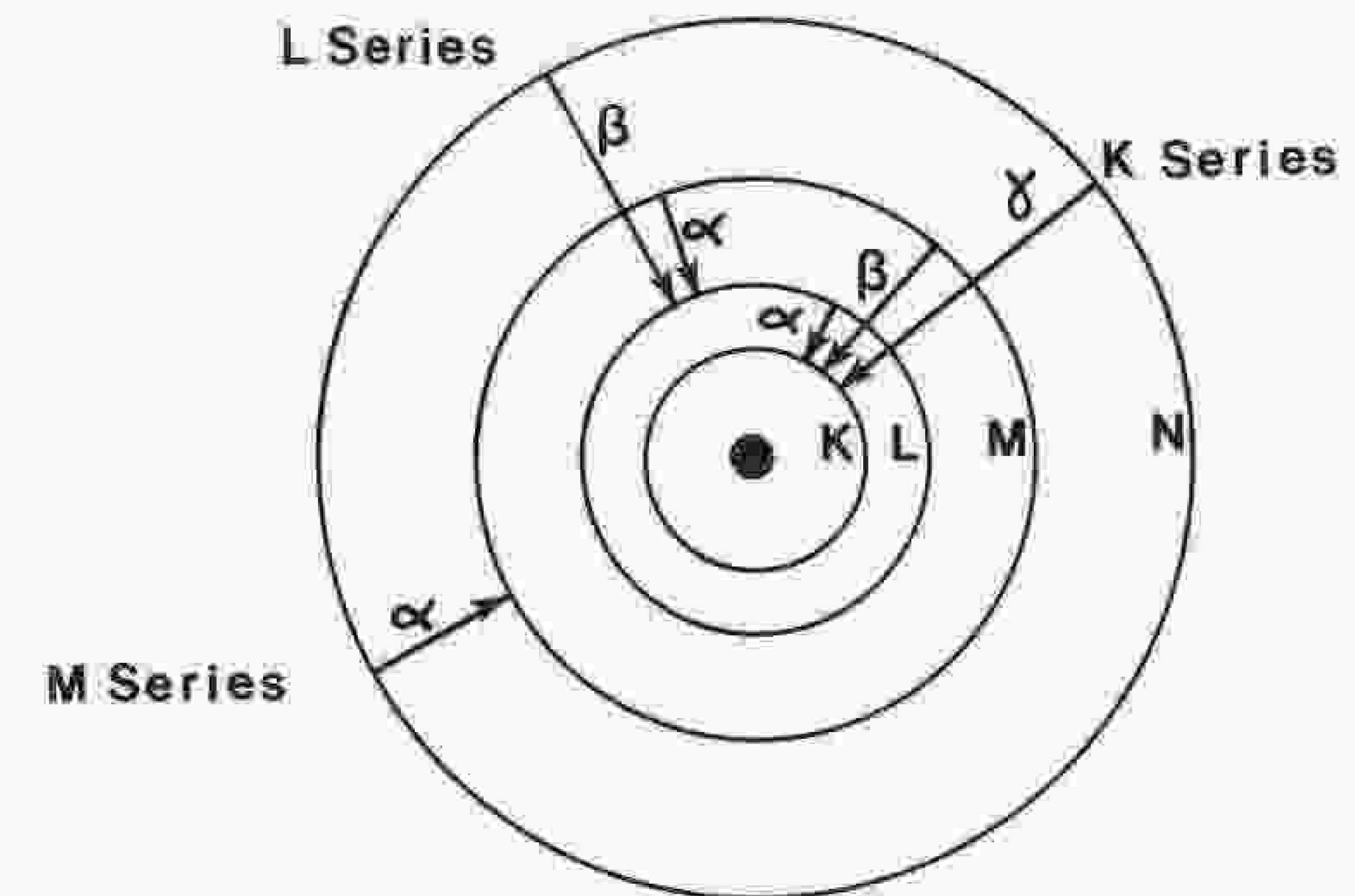
For example, $Cu_{K_{\alpha_1}}$ has an energy of 8.047 KeV. By substituting 8.047 into equation 3, the wavelength in Angstroms of $Cu_{K_{\alpha_1}}$ may be calculated:

$$\lambda = \frac{12.396}{8.047}$$

$$\lambda = 1.540 \text{ Å}$$

The relationships described in the above equations are useful in the identification and characterization of x-rays for elemental analysis. These equations are the basis for x-ray microprobe analysis.

Generation of an x-ray requires the removal of an electron from the inner shell of an atom. This removal may be accomplished in either of two ways. In



4-4. The spectrum of x-rays that may be generated from a single element.

the first, electromagnetic radiation (x-rays from an x-ray tube or a combination of gamma rays and x-rays from a radioactive source) is used to scatter specimen electrons, including those in the inner shells. The second method scatters specimen electrons utilizing a beam of charged particles such as the electrons found in the primary beam of the scanning electron microscope. For x-ray analysis in conjunction with scanning electron microscopy, electrons are preferable for production of specimen x-rays because the microscope produces a well-focused electron beam whose size (and thus the area analyzed) can be precisely controlled.

Removal of a specimen electron from its shell requires an energy expenditure by the impinging electron. To remove a specimen electron, the energy of the impinging electron must exceed the energy binding the specimen electron to that particular shell (binding energy). The minimum energy necessary to overcome the binding energy and to remove a specimen electron is termed the "critical energy." Use of an electron beam of lower energy than the critical energy will result in no specimen x-ray being produced. The critical energy varies from one shell to another and from one element to another.

Graphic representations of energy versus the probability of interaction between primary electrons and specimen electrons show the critical energy as a discontinuity termed an "absorption edge." The term absorption edge is often used in place of critical energy in x-ray tables. Production of specimen x-rays is optimized by the use of an electron beam whose energy is greater than, but close to, the absorption edge.

If the impinging electron is not able to remove a specimen electron (either by its having insufficient kinetic energy or by inelastic collisions), its deceleration will also result in the production of x-rays. These x-rays, however, are not characteristic of any element, but instead cover a broad, continuous spectrum and are termed "continuum x-rays" (Bremsstrählung or white radiation). The continuum x-rays are presently of no use in analytical electron microscopy.

Unfortunately, the characteristic spectrum is always superimposed on the continuous spectrum as shown in Figure 4-5.

ANALYSIS OF THE X-RAY SPECTRUM

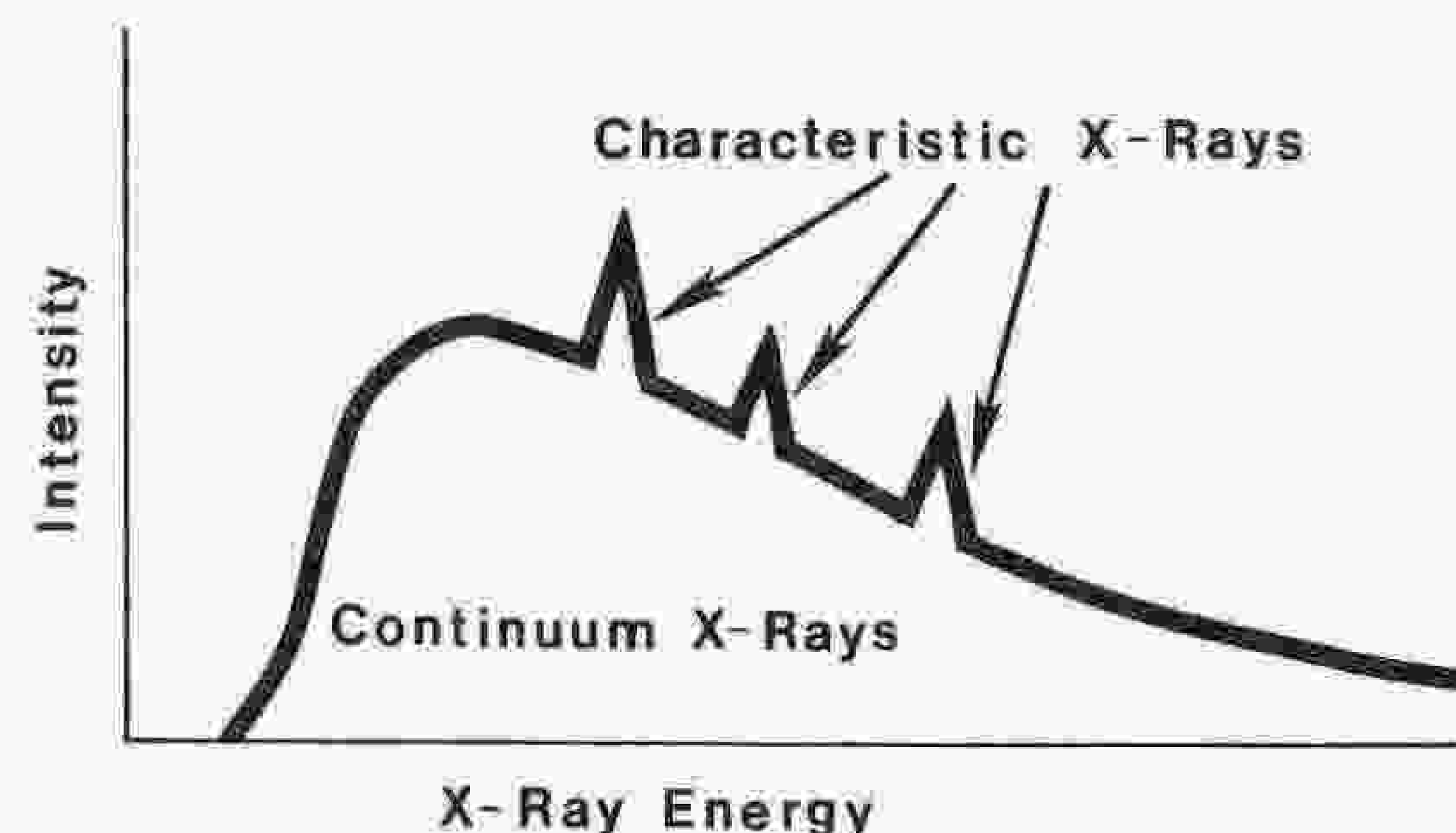
Previously, it was described that the interaction of an electron beam with a specimen in the scanning electron microscope produces many signals, including x-rays. Some of the x-rays produced in this manner have wavelengths and energies that are characteristic of the elements in that specimen. Elemental evaluation by the analytical microscopist may be accomplished using either of two fundamentally different x-ray analysis devices (13). Although the two systems may be considered competitive, they may tend to complement each other depending upon the application. These devices are the *Wavelength Dispersive Spectrometer (WDS)* and the *Energy Dispersive Spectrometer (EDS)*. The data presented in Table 4-1 presents the advantages afforded by both systems. It can be seen that either WDS, EDS, or both, may be useful in a particular application. Specifically, the EDS is useful in obtaining rapid qualitative analysis of an unknown sample while WDS is preferred for obtaining quantitative information and analysis of light or trace elements.

WAVELENGTH DISPERSIVE X-RAY ANALYSIS.

Detection and analysis of x-rays produced when an electron beam traverses a sample may be accomplished by the use of a wavelength dispersive spectrometer in conjunction with the scanning electron microscope. As the name would imply, this type of spectrometer identifies and counts the impinging x-rays based upon their characteristic wavelengths.

The energy of each x-ray photon emitted from a sample corresponds to the electron jump between shells in an atom. This relationship can be expressed as an equivalent wavelength where:

$$\lambda = \frac{hc}{E}$$



4-5. Demonstration of the characteristic x-ray spectrum superimposed on the continuum spectrum.

Table 4-1

COMPARISON OF EDS AND WDS

Advantages of Energy Dispersive Spectroscopy
*Compact, Low cost.
*Rapid (Qualitative analysis).
*Simultaneous multi-element analysis of the full x-ray spectrum (Na-upward).
*Display of the entire spectrum in digital format.
*High collection efficiency.
*Low sensitivity to geometric effects.
*Lack of higher-order lines which are generated in crystal diffraction.
*Digitally produced outputs for element line scans and distribution maps.

Advantages of Wavelength Dispersive Spectroscopy
*Higher inherent element separation (Resolution).
*High count rate on individual elements.
*Analysis can be highly quantitative.
*Better peak to background ratios.
*Analysis of a wide range of elements (Be to U).
*Higher sensitivity.
*Operates at room temperature.

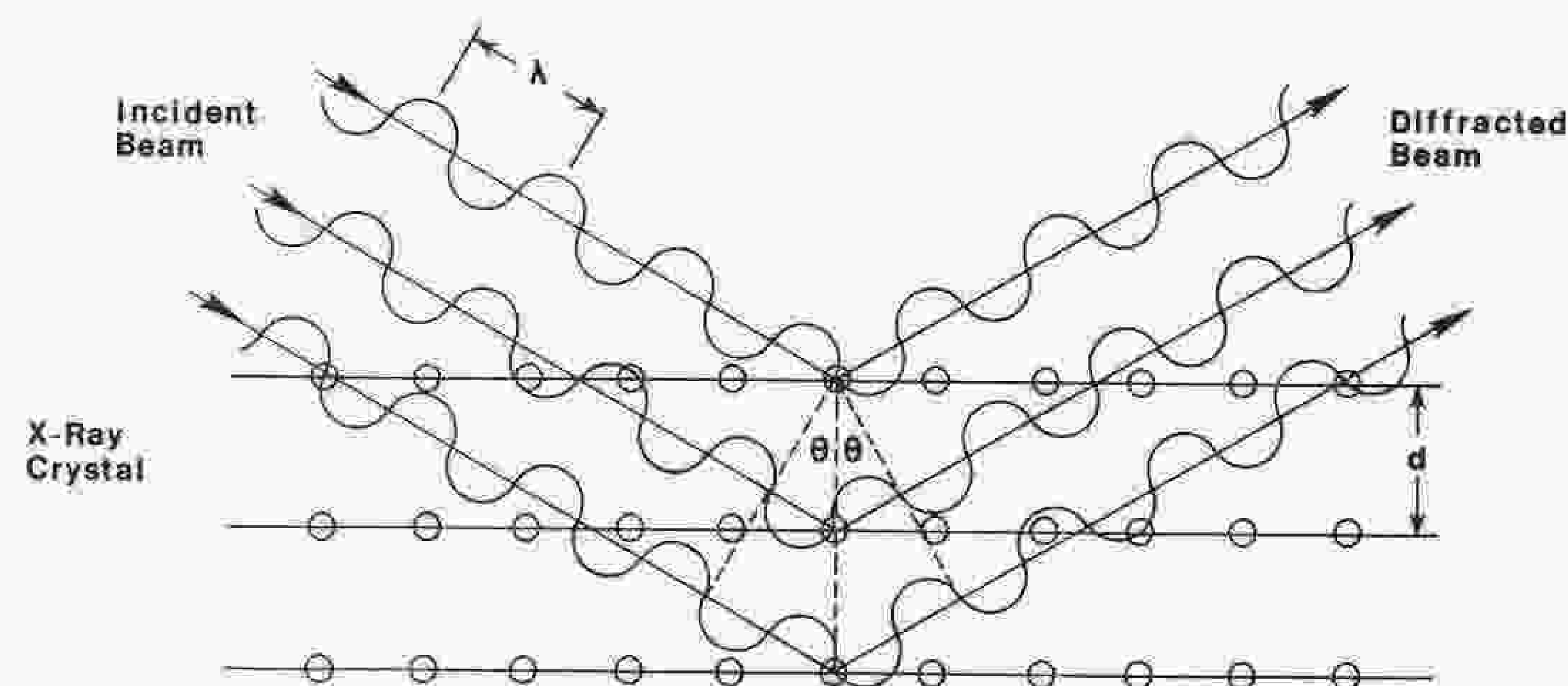
Each of the separate wavelengths can be segregated according to the phenomenon of diffraction. In the WDS system an x-ray analyzing crystal is used to separate or disperse the various x-rays allowing only a desired wavelength to be diffracted from the crystal to the x-ray detector for counting. Thus, the x-ray analyzing crystal and x-ray detector are the heart of the WDS system. The processing of the x-rays diffracted by the analysis crystal is accomplished by a detector using a proportional counter and signal processing by a preamplifier, amplifier, and pulse height analyzer.

ANALYSIS. When x-rays from the sample enter the lattice of a crystal, they are scattered by electrons in that crystal. This scattering is such that under certain conditions both constructive and destructive interference occurs. The constructive interference that results is what is commonly called x-ray diffraction (Fig. 4-6). X-ray diffraction will occur only if the wavelength of the impinging x-rays are incident at a specific angle (Θ) with respect to the interplanar spacing of a crystal (d). This phenomenon is expressed according to Bragg's Law:

$$n\lambda = 2d \sin \Theta$$

where:
λ = wavelength of diffracted x-rays
d = interplanar spacing of analysis crystal
Θ = angle between crystal surface and incident and diffracted x-rays
n = order of diffraction (1, 2, 3, . . .)

X-rays entering the analyzing crystal will be diffracted if they correctly fulfill the requirements imposed by Bragg's Law, or will not be diffracted, eventually being absorbed by the surroundings. Thus, the analysis crystal



4-6. Schematic representation of the diffraction of x-rays in a crystal.

serves as a device for sorting out and rejecting all x-rays present except for those specifically desired. Since the wavelength of the x-rays emitted for a particular element will be characteristic for that element alone, the wavelength sorting action of the crystal enables the presence of any element to be established. Unfortunately, not all of the conditions necessary to fulfill Bragg's Law are present in the interplanar spacing of one single crystal for all the elements. Thus, it is necessary to have a set of different crystals for various sections of the periodic table. Some of the commonly used crystals and their analytical ranges are listed in Table 4-2. There is an overlap in the wavelength detection range among the crystals useful in this type of analysis. The selection of particular crystals depends on the type of detector used, the type of analysis (e.g., qualitative vs. quantitative), and on the particular element being analyzed. For example, Pease and Elliot (13) note that while Ti_{K_α} x-rays may be detected by either a pentaerythritol (PET) crystal or lithium flouride (LiF) crystal, PET is a more efficient diffractor at the Ti_{K_α} wavelength and is more useful than LiF for qualitative displays such as area maps (discussed subsequently). LiF yields better resolution than PET and is thus more useful for most types of quantitative analysis of the titanium. In general, these crystals are easily interchanged without realignment of the system. A typical WDS system is shown in Figure 4-7.

The maintenance of the proper geometrical relationship between the x-ray source (the specimen), diffraction crystal, and detector is extremely important. The desired geometry can be accomplished by the use of either a semi-focusing (Johann) or a fully-focusing (Johansson) type of spectrometer (Fig. 4-8). In both systems the x-ray source, diffracting crystal and detector all lie on the circumference of a circle of specified radius termed the "Roland Circle." Further, the source-to-crystal distance must be equivalent to the crystal-to-detector distance for correct x-ray focusing at all times.

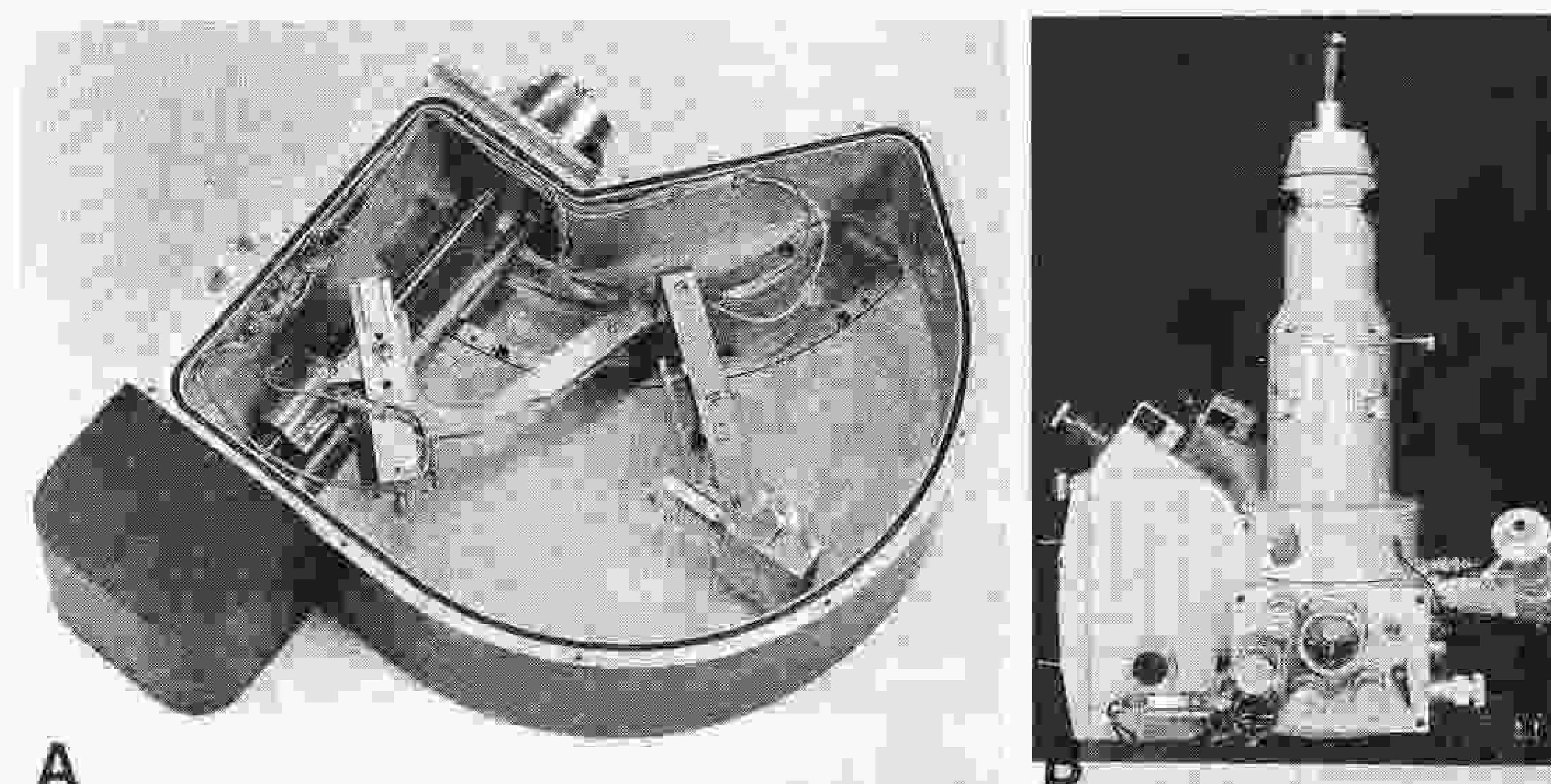
DETECTOR TYPES

Johann Semi-Focusing Spectrometer. The configuration of the crystal of the Johann (semi-focusing) type of detector (Fig. 4-8a) is such that the radius of curvature is twice that of the Roland circle. Thus, all of the diffracting surfaces do not lie on the circumference of this circle. Consequently, there is a certain degree of achromatic broadening of the focused x-ray beam occurring at the detector. This imposes limits upon the obtainable resolution of this type of spectrometer.

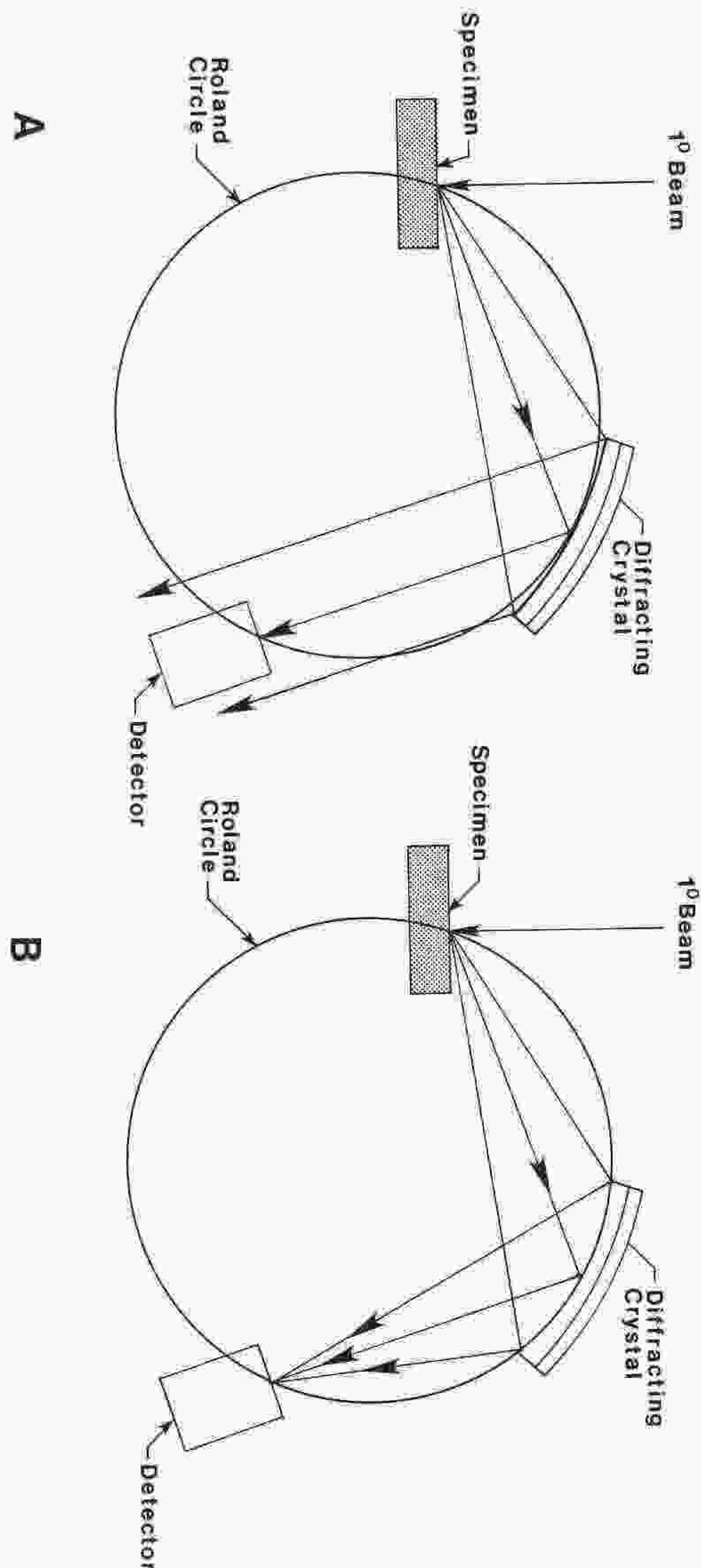
Johansson Fully-Focusing Spectrometer. A more efficient spectrometer geometry is found in the fully-focusing Johansson type (Fig. 4-8b) where the radius of curvature is equal to that of the Roland circle. In this design all diffracting surfaces lie on the circle. Thus, the achromatic broadening at the detector is eliminated, removing the resolution limitation imposed upon the Johann type spectrometer. Additionally, a second advantage found in the

Table 4-2

Crystal	Wavelength Range (nm)	Detectable Atomic Number Range K_α	L_α	M_α
Pb Stearate	0.50-1.50	4- 9	20-27	-
KAP	0.45-2.50	11-14	24-45	57-83
RbAP	0.20-1.80	11-14	26-64	57-92
Gypsum	0.26-1.50	11-14	28-57	59-92
ADP	0.18-1.03	12-21	33-67	65-92
EDT	0.14-0.83	14-22	37-75	70-92
PET	0.14-0.83	14-22	37-75	70-92
Ge	0.11-0.60	16-34	41-84	79-92
NaCl	0.09-0.53	16-37	43-92	82-92
LiF	0.10-0.38	19-35	49-88	-



4-7. Wavelength dispersive spectrometers. (A) Opened to show the internal components (Courtesy of ETEC). (B) Spectrometer in place on an SEM (Courtesy of JEOL).



4-8. Diagrammatic representation of the two types of wavelength dispersive spectrometers. (A) Johann semi-focusing spectrometer. (B) Johansson fully-focusing spectrometer.

Johansson geometry is that the linear relationship existing between the x-ray source-to-crystal distance and diffracted wavelength is fixed by design, therefore, crystal travel will always be proportional to the wavelength being diffracted.

SIGNAL PROCESSING. The x-rays, after being diffracted by the analysis crystal, may be detected by one of several devices, the most common being a proportional counter. A proportional counter is essentially a small metal chamber (cathode) with an anode wire at the center. X-rays enter and exit through windows along the tube. The tube is filled with a counting gas the nature of which depends upon the x-rays being detected. A 1000-2000V bias voltage is applied to the anode wire. When an x-ray enters the chamber, it will ionize a molecule of the proportional gas. The electron created by this ionizing event will be accelerated toward the anode. Traveling toward the anode, the electron will ionize other gas molecules resulting in a cascading effect. Due to this cascade the total charge finally collected at the anode may be 10^3 to 10^4 times the initial electron charge. Those electrons reaching the anode produce a measurable pulse in the bias voltage, the amplitude of which is directly proportional to the energy of the x-ray photon causing the pulse (hence the name proportional counter). This voltage pulse now representing the original x-ray photon is further amplified and processed.

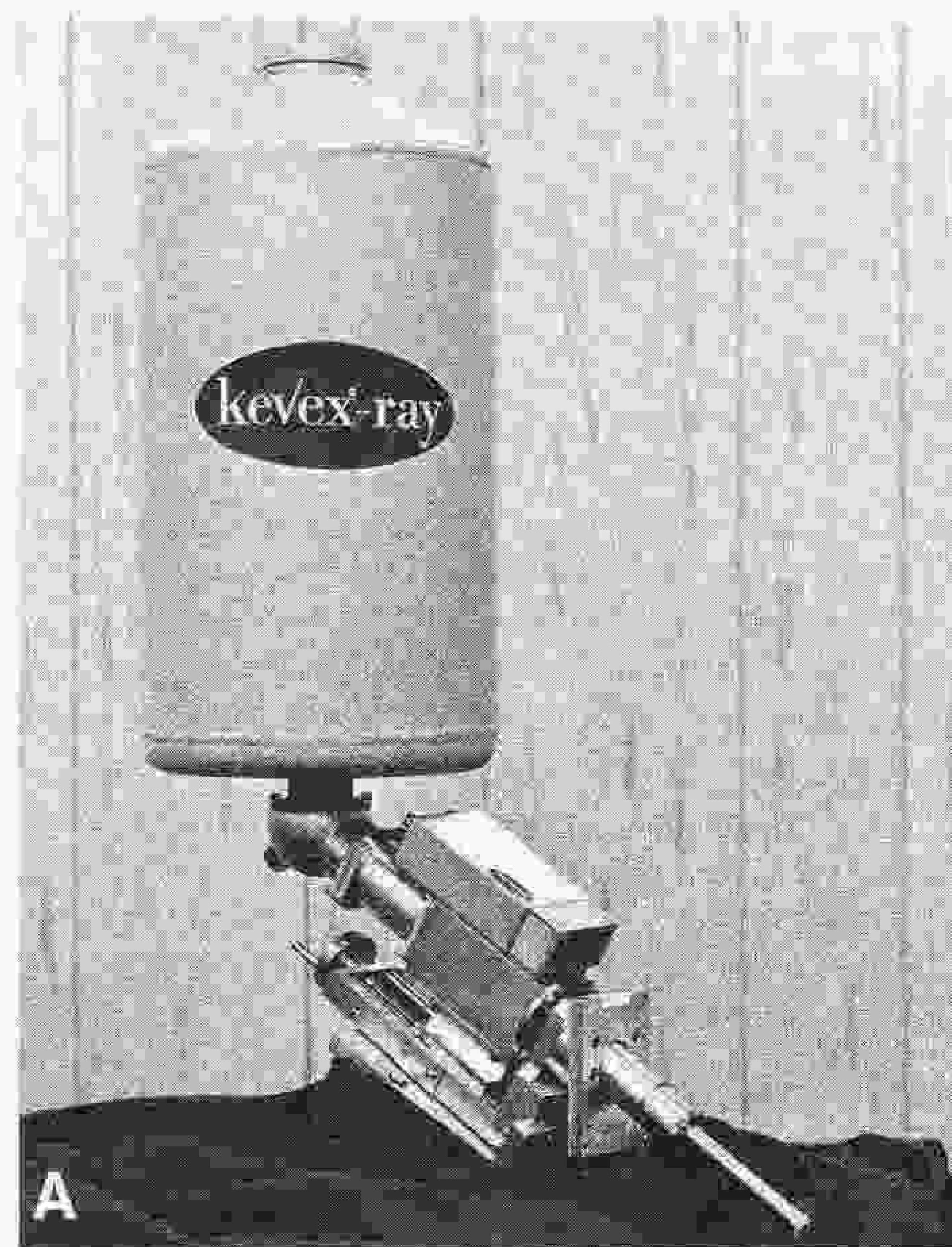
DATA ACCUMULATION. In an analysis using a wavelength dispersive system, the equipment is aligned in the Bragg geometry for the x-ray wavelength of a single pre-determined element. The number of x-ray counts reaching the detector during a specified period of analysis is recorded. This data may be compared to the counts obtained for the x-rays of other elements using the Bragg geometry for their respective wavelengths. In this manner, wavelength dispersive analysis can yield highly accurate quantitative information and may be used to produce qualitative displays (subsequently discussed).

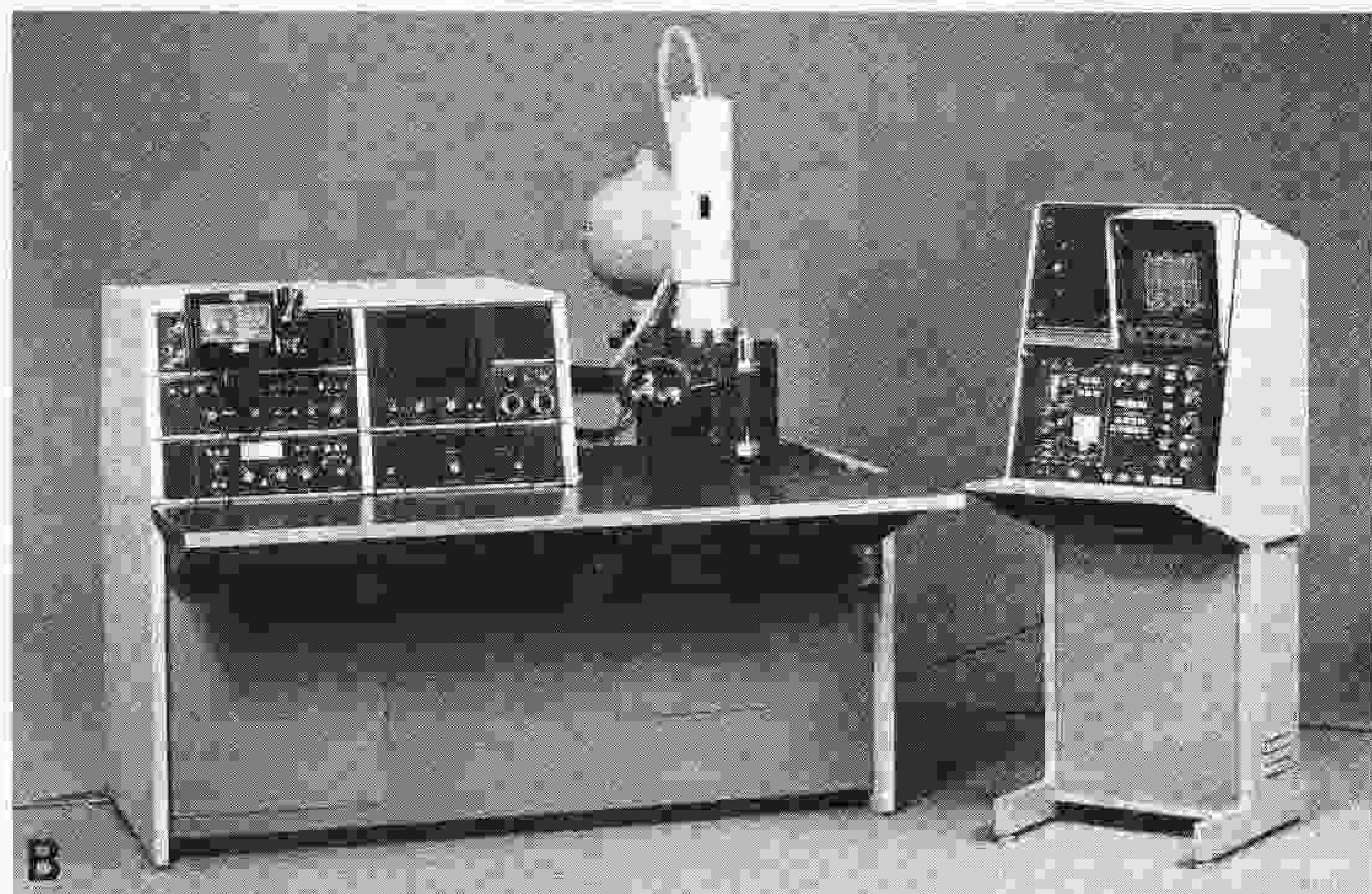
Wavelength dispersive spectroscopy is an extremely useful analytical tool providing highly accurate data of one element per spectrometer at one time. The energy dispersive spectrometer, on the other hand, is not limited in this manner and, therefore, is becoming the dominant x-ray analysis system used in scanning electron microscopy. The remainder of this chapter is devoted to the mechanics and applications of energy dispersive spectroscopy.

ENERGY DISPERSIVE X-RAY ANALYSIS

The x-rays produced in a scanning electron microscope include x-rays with energies characteristic of the elements in the specimen. X-ray energy analysis may be accomplished by energy dispersion which is the segregation of x-rays according to their energy.[1] While energy dispersion is possible using a flow proportional counter, the method currently preferred is dispersion with a semiconductor detector. A typical EDS system is shown in Fig. 4-9.

1. The term "non-dispersive" is also used to describe this type of x-ray analysis. Both terms are accurate because the energy of the x-rays is dispersed for display, but the x-rays themselves are not dispersed (diffracted) as in wavelength analysis.





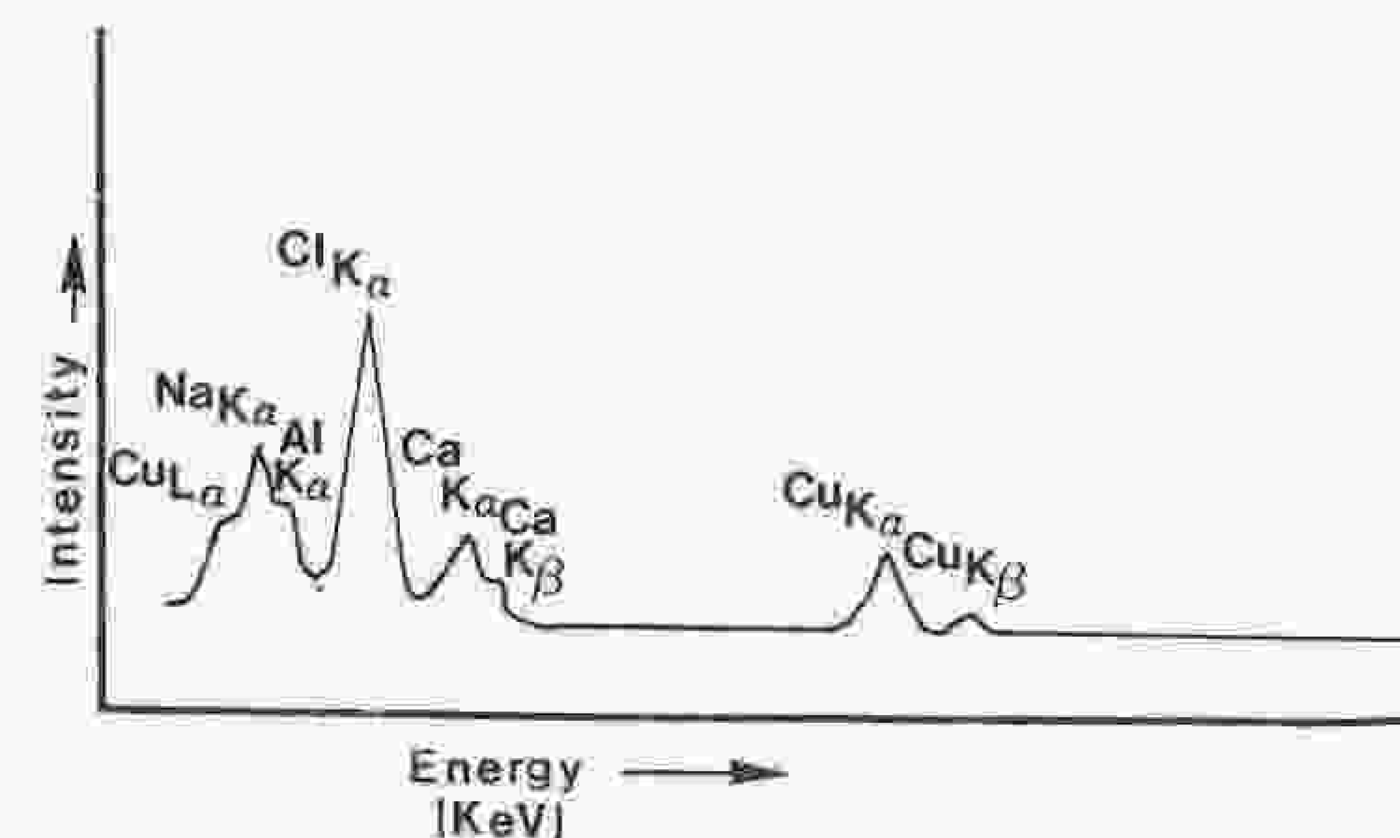
4-9. Energy dispersive spectrometer. (A) Energy dispersive spectrometer removed from microscope column (Courtesy of Kevex). (B) EDS in place on an SEM (Courtesy Phillips Electronic Instruments and EDAX).

When an x-ray strikes a semiconductor crystal, electrons in the crystal each absorb a given amount of energy. The greater the energy of the x-ray, the greater the number of electrons excited. The energy absorbed by the electrons is then converted to an electrical signal which is emitted and amplified. The strength of the current from the crystal is proportional to the x-ray energy. The amplified electrical pulses from the semiconductor are converted to digital form and fed into a multichannel analyzer (MCA) which sorts these signals and, in effect, counts the number of x-rays at each energy level which strike the crystal. This information is then plotted as shown in Figure 4-10 to form a representative spectrum.

THE SEMICONDUCTOR DETECTOR. The semiconductor detector crystal is the heart of the energy dispersive spectroscopy system. The detector is a piece of very pure semiconductor material. A semiconductor is a substance which is neither a good conductor of electricity nor a good insulator, but through which an electron may be passed with some difficulty. When a high voltage is passed through this material, it functions as a detector with the energy of impinging x-rays transferred to the electrical current in the crystal. Measuring the impulse of this current will allow the measurement of the x-ray energy.

The role of the crystal is the conversion of an electromagnetic signal (x-rays) to a purely electronic signal. Therefore, the crystal must have both extremely high charge-collection capabilities and extremely low carrier losses during the transmission of the signal through the crystal. Charge-carrier losses are minimized by the use of crystals that are nearly perfect. According to Goulding and Stone (9), imperfections in the crystal lattice will trap charge during transit and result in "leakage currents" with a subsequent signal reduction.

Only man-made crystals have the desired purity for use in semiconductor detectors. Silicon and germanium are the only crystal materials which have proven suitable for detectors, although cadmium telluride and silicon carbide may have use in the future (9). Even the purest man-made crystals have some impurities. The detrimental effects of impurities in the crystal lattice, described by Goulding and Stone (9), can be counteracted by the use of "lithium drifting."



4-10. An analysis spectrum obtained through the use of an energy dispersive spectrometer. Specimen is composed of copper, sodium, aluminum, chlorine and calcium.