
Diffraction and Spectrometer Measurements

7-1 INTRODUCTION

The x-ray spectrometer, briefly mentioned in Sec. 3-4, has had a long and uneven history in the field of x-ray diffraction. It was first used by W. H. and W. L. Bragg in their early work on x-ray spectra and crystal structure, but it then passed into a long period of relative disuse during which photographic recording in cameras was the most popular method of observing diffraction effects. The few spectrometers in use were all homemade and confined largely to the laboratories of research physicists. In the late 1940s, however, commercially made instruments became available; they rapidly became popular because they offered certain particular advantages over film techniques. Initially a research tool, the x-ray spectrometer has now become an instrument for control and analysis in a wide variety of industrial laboratories.

Depending solely on the way it is used, the basic x-ray spectrometer is really two instruments:

1. An instrument for measuring x-ray spectra by means of a crystal of known structure.
2. An instrument for studying crystalline (and noncrystalline) materials by measurements of the way in which they diffract x-rays of known wavelength.

The term *spectrometer* was originally used to describe both instruments, but, properly, it should be applied only to the first. The second instrument is aptly called a *diffractometer*: this name serves well to emphasize the particular use to which the instrument is being put, namely, diffraction analysis rather than spectrometry.

In this chapter, the design and operation of diffractometers will be described with particular reference to the commercial models available. Equipment suppliers are listed in [5.1], and Jenkins [G.37] gives worked-out examples of problems that arise in diffractometry. The best source of detailed information on diffractometer techniques is the book by Klug and Alexander [G.39].

Just as the emphasis in the present book is on diffraction rather than spectroscopy, the emphasis in this chapter is on the diffractometer. However, some experimental techniques used only, or mainly, in spectrometry are also described here, because they merge quite naturally with diffractometer techniques.

7-2 GENERAL FEATURES

In a diffraction camera, the intensity of a diffracted beam is measured through the amount of blackening it produces on a photographic film, a microphotometer measurement of the film being required to convert "amount of blackening" into x-ray intensity. In the diffractometer, the intensity of a diffracted beam is measured directly by an electronic *counter*. There are many types of counters, but they all convert incoming x-rays into surges or pulses of electric current in the circuit connected to the counter. This circuit counts the number of current pulses per unit of time, and this number is directly proportional to the intensity of the x-ray beam entering the counter. (Logically, the device known as a counter should be called a "detector," and the counting circuit a "counter," but the detecting, pulse-producing device is usually called a counter.)

Basically, a diffractometer is designed somewhat like a Debye-Scherrer camera, except that a movable counter replaces the strip of film. In both instruments, essentially monochromatic radiation is used and the x-ray detector (film or counter) is placed on the circumference of a circle centered on the powder specimen. The essential features of a diffractometer are shown in Fig. 7-1. A powder specimen *C*, in the form of a flat plate, is supported on a table *H*, which can be rotated about an axis *O* perpendicular to the plane of the drawing. The x-ray source is *S*, the line focal spot on the target *T* of the x-ray tube; *S* is also normal to the plane of the drawing and therefore parallel to the diffractometer axis *O*. X-rays diverge from this source and are diffracted by the specimen to form a convergent diffracted beam which comes to a focus at the slit *F* and then enters the counter *G*. *A* and

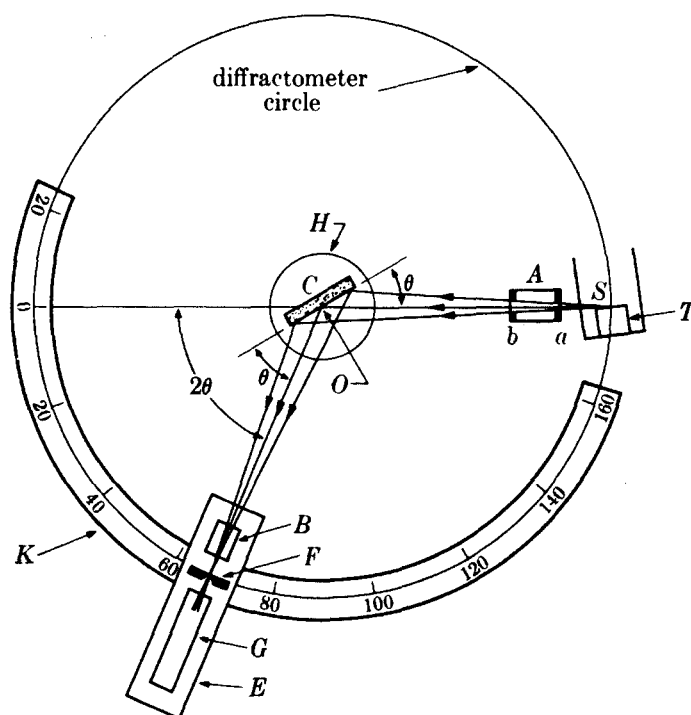


Fig. 7-1 X-ray diffractometer (schematic).

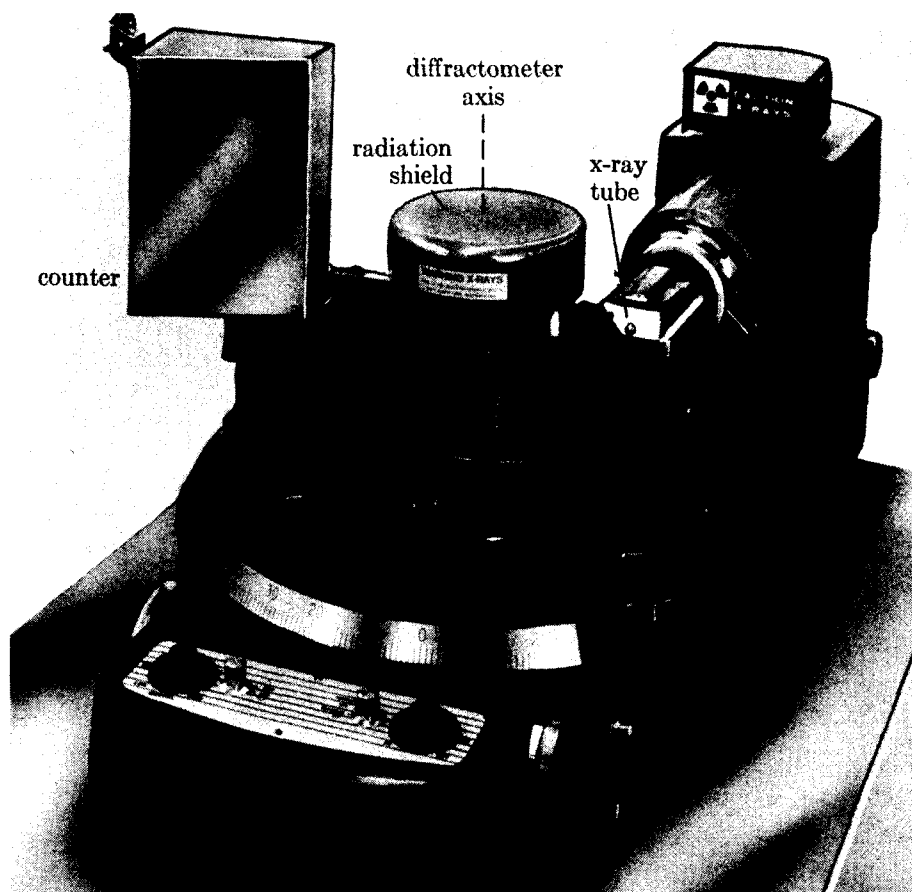


Fig. 7-2(a) Diano diffractometer. (Courtesy of Diano Corporation. This company has, since 1972, manufactured and sold the x-ray diffraction and spectroscopy equipment formerly made by the General Electric Company.)

B are special slits which define and collimate the incident and diffracted beams. The filter is usually placed in a special holder (not shown) in the diffracted, rather than the incident, beam; a filter in the diffracted beam not only serves its primary function (suppression of $K\beta$ radiation) but also decreases background radiation originating in the specimen.

The receiving slits and counter are supported on the carriage E , which may be rotated about the axis O and whose angular position 2θ may be read on the graduated scale K . The supports E and H are mechanically coupled so that a rotation of the counter through $2x$ degrees is automatically accompanied by rotation of the specimen through x degrees. This coupling ensures that the angles of incidence on, and reflection from, the flat specimen will always be equal to one another and equal to half the total angle of diffraction, an arrangement necessary to preserve focusing conditions. The counter may be power-driven at a constant angular velocity about the diffractometer axis or moved by hand to any desired angular position.

Figures 7-2 and 7-3 illustrate three commercial instruments. Basically, they all adhere to the design principles described above, but they differ in detail and

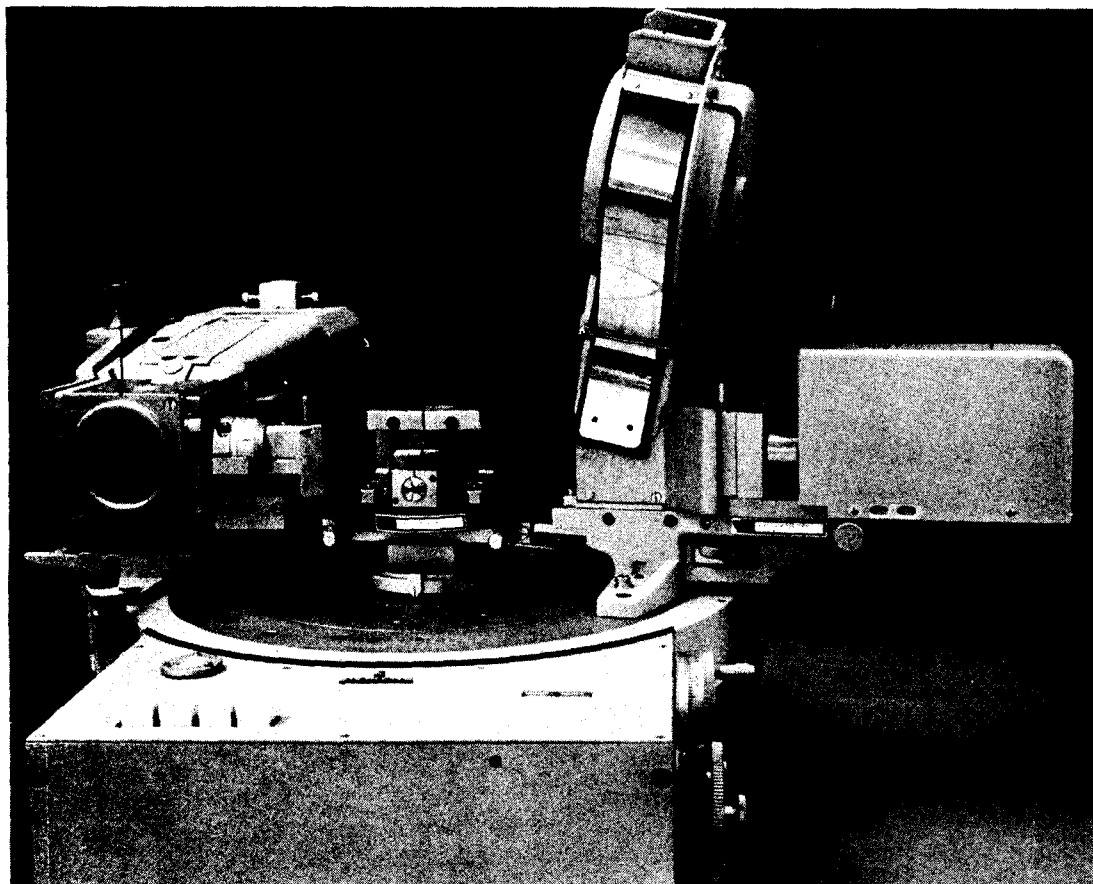


Fig. 7-2(b) Siemens diffractometer. The radiation shield has here been raised from its normal position covering the specimen. (Courtesy of Siemens Corporation.)

in positioning. In the Diano and Siemens instruments shown in Fig. 7-2(a) and (b), the diffractometer axis is vertical and the counter moves in a horizontal plane. The axis of the Philips diffractometer (Fig. 7-3) is horizontal and the counter moves in a vertical plane.

The way in which a diffractometer is used to measure a diffraction pattern depends on the kind of circuit used to measure the rate of production of pulses in the counter. The pulse rate may be measured in two different ways:

1. The succession of current pulses is converted into a steady current, which is measured on a meter called a *counting-rate meter*, calibrated in such units as counts (pulses) per second (c/s or cps). Such a circuit gives a continuous indication of x-ray intensity.
2. The pulses of current are counted electronically in a circuit called a *scaler*, and the average counting rate is obtained simply by dividing the number of pulses counted by the time spent in counting. This operation is essentially discontinuous because of the time spent in counting, and a scaling circuit cannot be used to follow continuous changes in x-ray intensity.

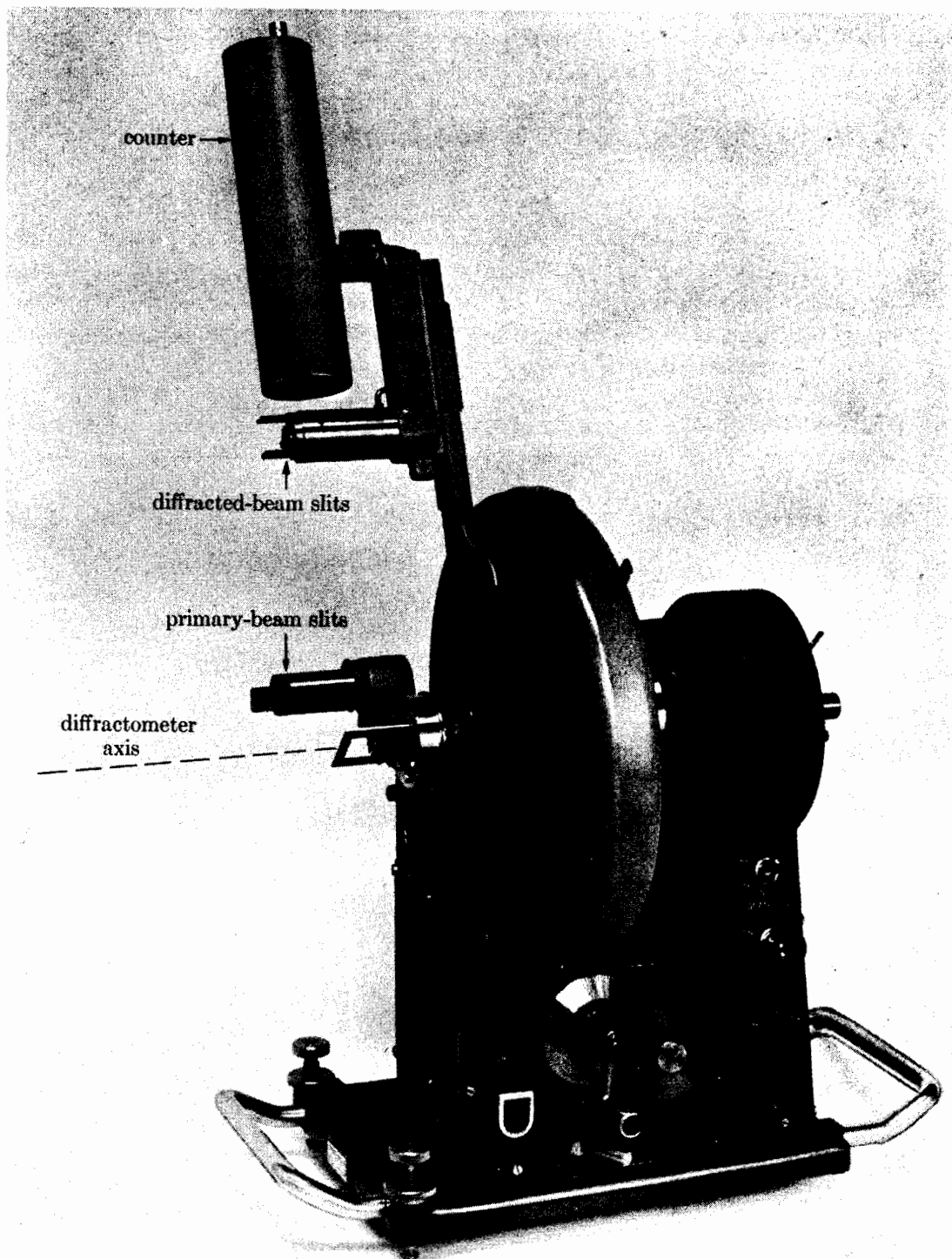


Fig. 7-3 Philips diffractometer. The window of a vertical x-ray tube, not shown, would be immediately behind the primary-beam slits. Radiation shield not shown. See also Fig. 15-10. (Courtesy of Philips Electronic Instruments, Inc.)

Corresponding to these two kinds of measuring circuits, there are two ways in which the diffraction pattern of an unknown substance may be obtained with a diffractometer (Fig. 7-4):

1. *Continuous.* The counter is set near $2\theta = 0^\circ$ and connected to a counting-rate meter. The output of this circuit is fed to a strip-chart recorder. The counter is then driven at a constant angular velocity through increasing values of 2θ until the whole angular range is "scanned." At the same time, the paper chart on the recorder moves at a constant speed, so that distances along the length of the chart are proportional to 2θ . The result is a chart, such as Fig. 7-5, which gives a record of counts per second (proportional to diffracted intensity) vs. diffraction angle 2θ . A "high" scanning speed is typically 2° of 2θ per minute; at this rate a complete scan extending from, say, 10° to 160° 2θ , requires $150/2 = 75$ minutes. (The upper limit of counter motion, determined by contact between counter and x-ray tube, is about 165° 2θ .)

2. *Intermittent.* The counter is connected to a scaler and set at a fixed value of 2θ for a time sufficient to make an accurate count of the pulses obtained from the counter. The counter is then moved to a new angular position and the operation repeated. The range of 2θ of interest is covered in this fashion, and the curve of intensity vs. 2θ is finally plotted by hand. When the continuous background between diffraction lines is being measured, the counter may be moved in steps of several degrees, but determinations of line profile may require measurements of intensity at angular intervals as small as 0.01° . This method of obtaining a diffraction

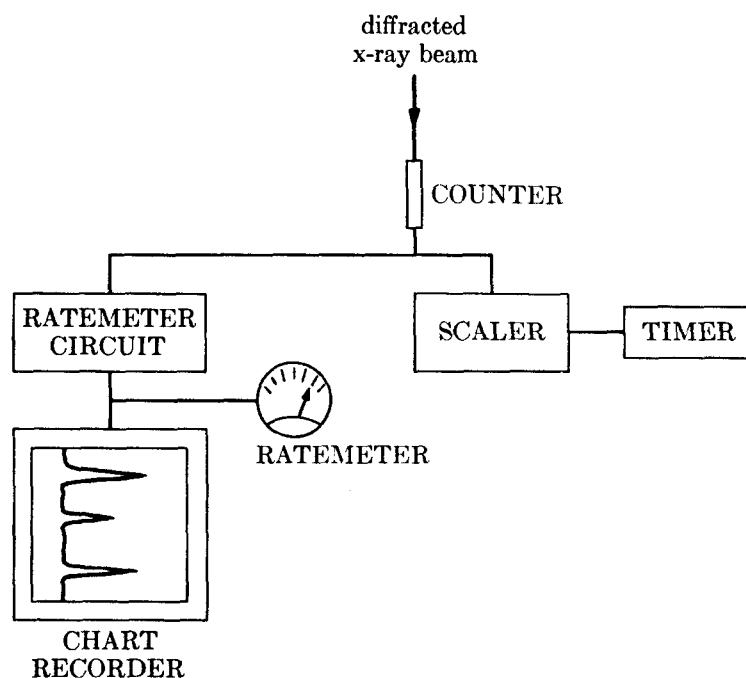


Fig. 7-4 Block diagram of detector circuits for a diffractometer. The ratemeter circuit actuates a meter, for a visual indication of the counting rate, and a chart recorder. The scalar and timer operate together.

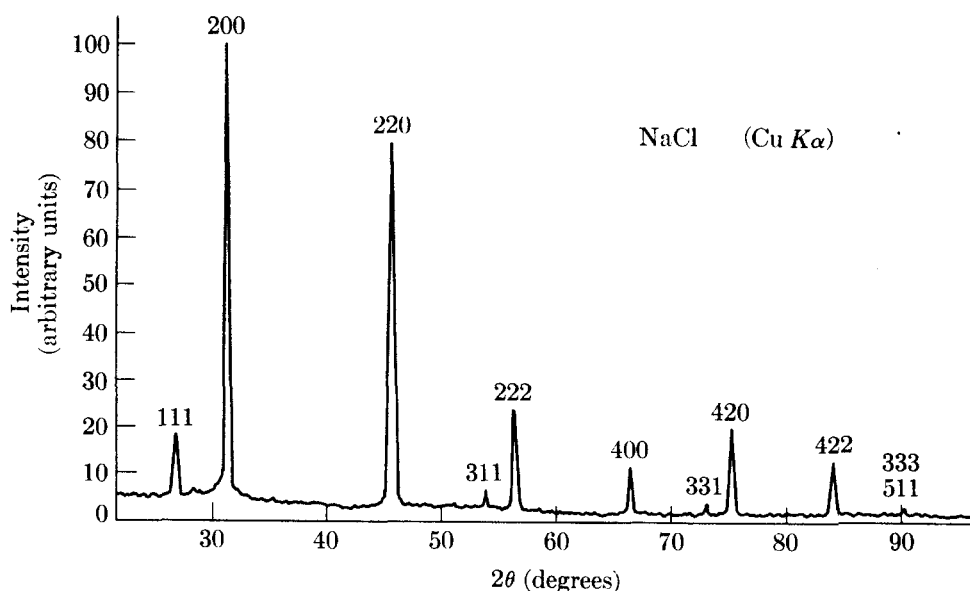


Fig. 7-5 Automatically recorded diffraction pattern of NaCl powder. Copper radiation, nickel filter. About half of the entire range of 2θ is shown here. The numbers on the ordinate are simply chart units, which may be converted to counts/sec if desired. Warren [G.30].

pattern is much slower than that involving a ratemeter and recorder but it yields more precise measurements of intensity. This operation may be performed automatically with some diffractometers (see below).

There is a fundamental difference between the operation of a powder camera and a diffractometer. In a camera, all diffraction lines are recorded simultaneously, and variations in the intensity of the incident x-ray beam during the exposure can have no effect on relative line intensities. On the other hand, with a diffractometer, diffraction lines are recorded one after the other, and it is therefore imperative to keep the incident-beam intensity constant when relative line intensities must be measured accurately. Since the usual variations in line voltage are quite appreciable, the x-ray tube circuit of a diffractometer must include a voltage stabilizer and a tube-current stabilizer.

The kind of specimen used depends on the kind of material available. Flat metal sheet or plate may be examined directly; however, such materials almost always exhibit preferred orientation and this fact must be kept in mind in assessing relative intensities. This is also true of wires, which are best examined by cementing a number of lengths side by side to a glass plate. This plate is then inserted in the specimen holder so that the wire axes are at right angles to the diffractometer axis. Powder specimens are best prepared by placing the powder in a recess in a glass or plastic plate, compacting it under just sufficient pressure to cause cohesion without use of a binder, and smoothing off the surface. Too much pressure causes preferred orientation of the powder particles. Alternatively, the powder may be mixed with a binder and smeared on the surface of a glass slide. The powder should be ground extremely fine, to a size of 10 microns or less, if relative line intensities are to be accurately reproducible; since the flat specimen is not rotated

as a Debye-Scherrer specimen is, the only way of obtaining an adequate number of particles having the correct orientation for reflection is to reduce their average size. (Specimen "spinners" are available to continuously rotate the specimen in its own plane. But this kind of rotation is not nearly as effective, in bringing new orientations into the beam, as the kind that takes place in a Debye-Scherrer camera.) Surface roughness also has a marked effect on relative line intensities. If the surface is rough, as in the case of a coarse powder compact, and the linear absorption coefficient high, the intensities of low-angle reflections will be abnormally low because of the absorption of the diffracted rays in each projecting portion of the surface. The only way to avoid this effect is to use a flat-surfaced compact of very fine powders or a specimen with a polished surface.

Single-crystal specimens may also be examined in a diffractometer by mounting the crystal on a three-circle goniometer, such as that shown in Fig. 5-7, which will allow independent rotation of the specimen and counter about the diffractometer axis and two other axes passing through the specimen. (Incidentally, independent rotation of the specimen about the diffractometer axis is often called an ω , rather than a θ , rotation.) In fact, special *single-crystal diffractometers* are available, designed solely for the determination of complex crystal structures.

A diffractometer may be used for measurements at high or low temperatures by surrounding the specimen with the appropriate heating or cooling unit. Such an adaptation of the instrument is much easier with the diffractometer than with a camera because of the generally larger amount of free working space around the specimen in the former. An additional advantage is that dynamic measurements may be made. For example, the counter may be set to receive a prominent line of a phase stable only at room temperature; as the temperature is continuously increased, the ratemeter will continuously indicate and record the disappearance of that phase, in the form of a curve of line intensity vs. temperature.

Automatic diffractometers have been made by many investigators by modifying conventional instruments, and they are also available from manufacturers as original equipment [7.1 to 7.7]. Automation requires mechanical modifications to permit (1) automatic specimen changing and (2) step scanning. The latter allows the counter to be driven quickly from one angular position 2θ to another, pausing at each position long enough for the scaler to make an accurate count. Specimen and counter movements are controlled by a computer which permits, for example, a step scan over any selected range of 2θ in steps of any desired size. The scaler output (diffracted x-ray intensity) and the angle to which it refers may be printed by a teletypewriter, punched on paper tape, or stored on magnetic tape. A computer can then process the output data in various ways, depending on the problem involved. This kind of automation can result in continuous, unattended, day-and-night operation of a diffractometer.

In the succeeding sections, the various parts of the diffractometer will be described in greater detail. This summary of the general features of the instrument is enough to show its principal advantage over the powder camera: the quantitative measurement of line position and intensity is made in one operation with a diffractometer, whereas the same measurement with film technique requires at least two steps (recording the pattern on film and making a microphotometer

record of the film) and leads to an over-all result which is generally of lower accuracy. This superiority of the diffractometer is reflected in the much higher cost of the instrument, a cost due not only to the precision machining necessary in its mechanical parts but also to the expensive circuits needed to stabilize the power supply and measure the intensity of diffracted beams.

The diffractometer is a superb instrument for dealing with many problems. But it is not without its faults. A counter "sees" only the radiation it is exposed to and is blind to all diffracted and scattered rays not lying in the plane of the diffractometer circle. A photographic film, with an area of several square inches, will intercept and record a great many rays, disclosing at a glance such conditions as coarse grains and preferred orientation (Chap. 9); a diffractometer does not immediately see these things. As Guinier [G.21] puts it, "The photographic method is admirably suited to the *qualitative exploration of an unknown pattern*, since one can then find totally unexpected phenomena. The counter is necessary for *quantitative measurements* on a pattern which is already known qualitatively."

7-3 X-RAY OPTICS

The chief reason for using a flat specimen is to take advantage of the focusing action described in Sec. 6-6 and so increase the intensity of weak diffracted beams to a point where they can be accurately measured. Figure 7-6 shows how this is done. For any position of the counter, the receiving slit F and the x-ray source S are always located on the diffractometer circle, which means that the face of the specimen, because of its mechanical coupling with the counter, is always tangent to a focusing circle centered on the normal to the specimen and passing through F and S . The focusing circle is not of constant size but increases in radius as the angle 2θ decreases, as indicated in Fig. 7-6. Perfect focusing at F requires that the specimen be curved to fit the focusing circle. Use of a flat specimen causes some broadening of the diffracted beam at F and a small shift in line position toward smaller angles, particularly at 2θ angles less than about 60° ; both effects can be lessened by decreasing the divergence of the incident beam, at the expense

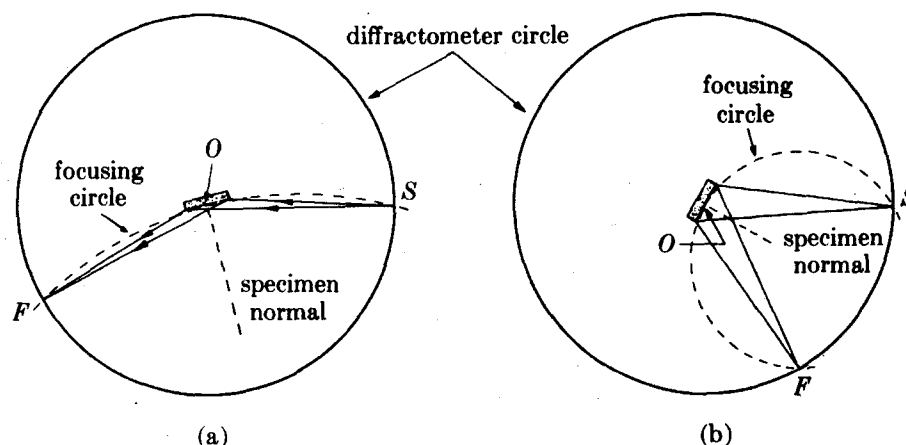


Fig. 7-6 Focusing geometry for flat specimens in (a) forward reflection and (b) back reflection.

of decreased intensity. (Neither focusing nor intensity has to be sacrificed if the specimen surface always conforms to the focusing circle. A device to do this is commercially available, based on a design by Ogilvie [7.24]. The powder specimen is mounted on a thin flexible strip, which is automatically bent to the proper curvature at each angle 2θ .)

The line source S extends considerably above and below the plane of the drawing of Fig. 7-6 and emits radiation in all directions, but the focusing described above requires that all rays in the incident beam be parallel to the plane of the drawing. This condition is realized as closely as possible experimentally by passing the incident beam through a *Soller slit* (Fig. 7-7), slit A in Fig. 7-1, which contains a set of closely spaced, thin metal plates parallel to the plane of the diffractometer circle. These plates remove a large proportion of rays inclined to the plane of the diffractometer circle and still allow the use of a line source of considerable length. Typical dimensions of a Soller slit are: length of plates 32 mm, thickness of plates 0.05 mm, clear distance between plates 0.43 mm. At either end of the slit assembly are rectangular slits a and b , the entrance slit a next to the source being narrower than the exit slit b . The combination of slits and plates breaks up the incident beam into a set of triangular wedges of radiation, as indicated in Fig. 7-7. There are, of course, some rays, not shown in the drawing, which diverge in planes perpendicular to the plane of the plates, and these rays cause the wedges of radiation to merge into one another a short distance away from the exit slit. However, the long, closely spaced plates do restrict this unwanted divergence to an angle of about 1.5° . Slits a and b define the divergence of the incident beam in the plane of the diffractometer circle. The slits commonly available have divergence angles ranging from very small values up to about 4° . In the forward-reflection region, a divergence angle of 1° is sufficient because of the low inclination of the specimen surface to the incident beam, but in back reflection an increase in divergence angle to 3 or 4° will increase the area irradiated and the diffracted intensity. But if line intensities are to be compared over the whole range of 2θ , the same divergence must be used throughout and the specimen must be wider than the beam at all angles.

The beam diffracted by the specimen passes through another Soller slit and the receiving slit F before entering the counter (Fig. 7-8). Since the receiving slit defines the width of the beam admitted to the counter, an increase in its width will increase the maximum intensity of any diffraction line being measured but at the expense of some loss of resolution. On the other hand, the relative *integrated intensity* of a diffraction line is independent of slit width, which is one reason for its greater fundamental importance.*

* A number of things besides slit width (e.g., x-ray tube current) will change the integrated intensity of a single diffraction line. The important thing to note, however, is that a change in any one of the operating variables changes the integrated intensities of all diffraction lines in the same ratio but can produce very unequal effects on maximum intensities. Thus, if I_1/I_2 is the ratio of the integrated intensities of two lines measured with a certain slit width and M_1/M_2 the ratio of their maximum intensities, then another measurement with a different slit width will result in the same ratio I_1/I_2 for the integrated intensities, but the ratio of the maximum intensities will now, in general, differ from M_1/M_2 .

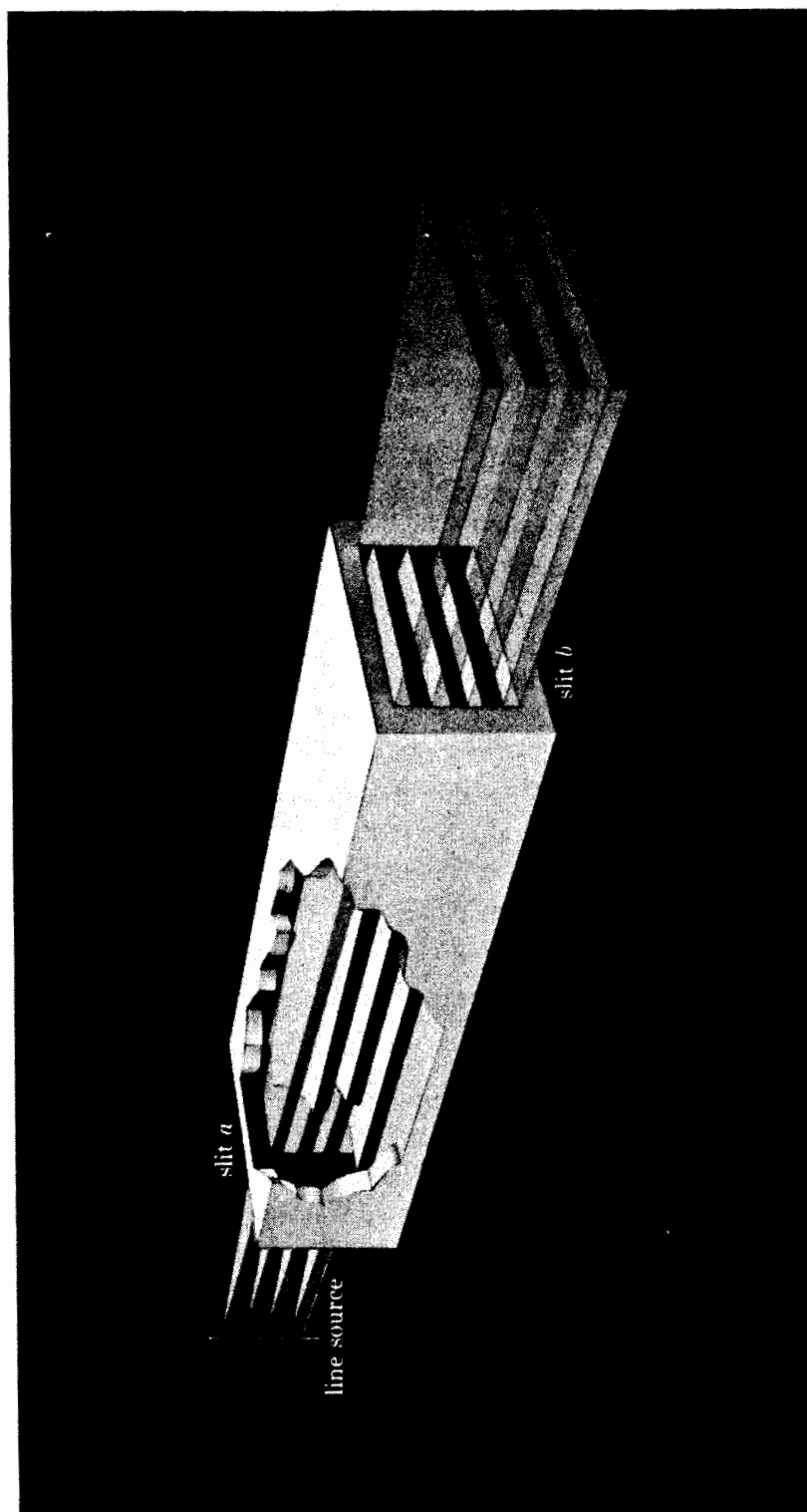


Fig. 7-7 Soller slit (schematic). For simplicity, only three metal plates are shown; actual Soller slits contain about a dozen.

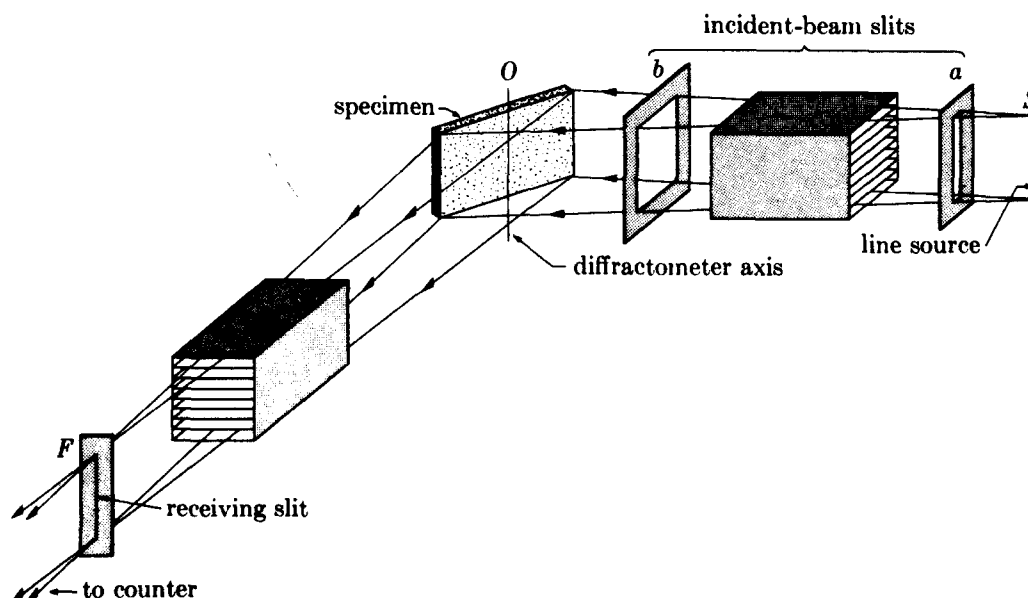


Fig. 7-8 Arrangement of slits in diffractometer.

Because of the focusing of the diffracted rays and the relatively large radius of the diffractometer circle, about 15 cm in commercial instruments, a diffractometer can resolve very closely spaced diffraction lines. Indicative of this is the fact that resolution of the Cu $K\alpha$ doublet can be obtained at 2θ angles as low as about 40° . Such resolution can only be achieved with a correctly adjusted instrument, and it is necessary to so align the component parts that the following conditions are satisfied for all diffraction angles:

1. line source, specimen surface, and receiving-slit axis are all parallel,
2. the specimen surface coincides with the diffractometer axis, and
3. the line source and receiving slit both lie on the diffractometer circle.

7-4 COUNTERS (GENERAL)

Without exception all electronic counters were developed by nuclear physicists for studies of radioactivity. They can detect not only x - and γ -radiation, but also charged particles such as electrons and α -particles, and the design of the counter and associated circuits depends to some extent on what is to be detected. Here we are concerned only with counters for the detection of x -rays of the wavelengths commonly encountered in diffraction.

Four types of counters are currently in use: proportional, Geiger, scintillation, and semiconductor. All depend on the power of x -rays to ionize atoms, whether they are atoms of a gas (proportional and Geiger counters) or atoms of a solid (scintillation and semiconductor counters). A general treatment of the first three types has been given by Parrish [7.8].

We will be interested in three aspects of counter behavior: losses, efficiency, and energy resolution. These are defined below and made more specific in later sections on particular counters.

Counting Losses

The absorption of a quantum (photon) of x-rays in the active volume of a counter causes a voltage pulse in the counter output. Pulses from the counter then enter some very complex electronic circuitry, consisting of one or more pulse amplifiers, pulse shapers, etc. and, at the end, a scaler or ratemeter and, possibly, a pulse-height analyzer (Sec. 7-9). Let us call all the circuitry beyond the counter simply the "electronics." Then we are interested not simply in the behavior of the counter alone, but in the behavior of the whole system, namely, the counter-electronics combination.

If the x-ray beam to be measured is strong, the rate of pulse production in the counter will be high, and the counting rate given by the ratemeter will be high. (Roughly speaking, several thousand counts per second is a "high" rate in powder diffractometry, and less than a hundred cps a "low" rate.) As the counting rate increases, the time interval between pulses decreases and may become so small that adjacent pulses merge with one another and are no longer resolved, or counted, as separate pulses. At this point counting loss has begun. The quantity that determines this point is the *resolving time* t_s of the counter-electronics system, defined as the minimum time between two resolvable pulses.

The arrival of x-ray quanta at the counter is random in time. Therefore pulse production in the counter is random in time, and a curve showing the change in voltage of the counter output would look like Fig. 7-9. If the arrival and absorption of entering quanta were absolutely periodic in time, the maximum counting rate without losses would be given simply by $1/t_s$. But even if their average rate of arrival is no greater than $1/t_s$, some successive quanta may be spaced less than t_s apart because of their randomness in time. It follows that counting losses will occur at rates less than $1/t_s$ and that losses will increase as the rate increases, as shown in Fig. 7-10. Here "quanta absorbed per second" are directly proportional to the x-ray intensity, so that this curve has an important bearing on diffractometer measurements, because it shows the point at which the observed counting rate is no longer proportional to the x-ray intensity. The straight line shows the ideal response that can be obtained with a proportional counter at the rates shown. This linear, no-loss behavior is fortunately typical of most counters used today in diffractometry; otherwise one would have the tedious task of correcting some observed counting rates for losses.

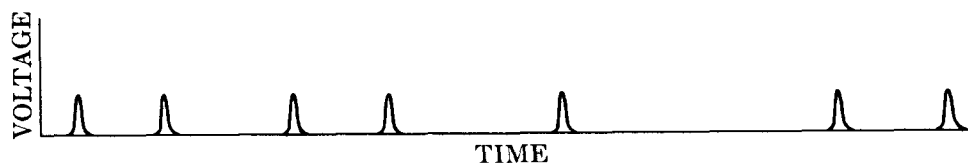


Fig. 7-9 Randomly spaced voltage pulses produced by a counter.

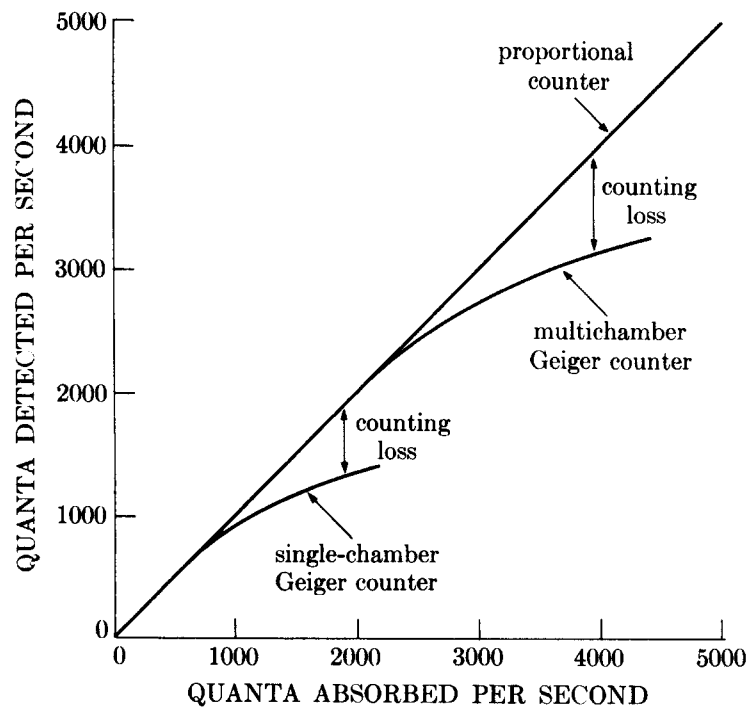


Fig. 7-10 The effect of counting rate on counting losses for three kinds of counter (schematic).

If the resolving time t_s of the counter-electronics is known, the point at which losses begin can be calculated by an easily remembered rule: a loss of one percent occurs at a rate of about one percent of $1/t_s$. Thus, if t_s is one microsecond, the counting rate should be linear to within one percent up to a rate of about 10,000 cps.

Ordinarily, the resolving time is unknown. But if nonlinear counting behavior is suspected, the counting rate at which losses begin can be determined experimentally by the following procedure. Position the counter to receive a strong diffracted beam, and insert in this beam a sufficient number of metal foils of uniform thickness to reduce the counting rate almost to the cosmic background. (Cosmic rays, because of their high penetrating power, pass right through the walls of the counter and continually produce a few counts per second.) Measure the counting rate, remove one foil, measure the counting rate, and continue in this manner until all the foils have been removed. Because each foil produces the same fractional absorption of the energy incident on it, a plot of observed counting rate (on a logarithmic scale) vs. number of foils removed from the beam (on a linear scale) will be linear up to the point where losses begin and will in fact resemble Fig. 7-10. A curve of this kind is shown in Fig. 7-11.

Counting Efficiency

The overall efficiency E of the counter-electronics system in detecting incident x-ray quanta as resolved pulses is the product of the absorption efficiency E_{abs} and the detection efficiency E_{det} .

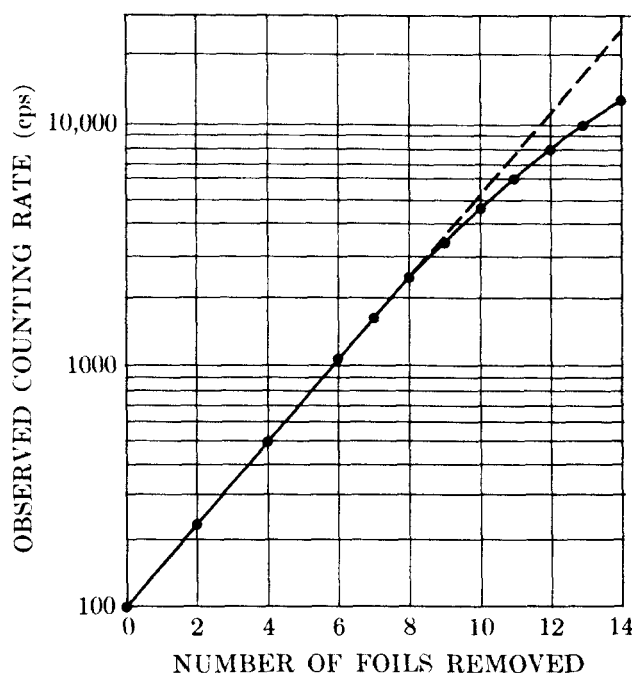


Fig. 7-11 Calibration curve of a multichamber Geiger counter. Cu $K\alpha$ radiation. Nickel foils, each 0.01 mm thick, used as absorbers.

All counters have a thin “window,” usually of mica or beryllium, through which the x-rays must pass before reaching the active volume of the counter. The fraction of the incident radiation absorbed by the window $f_{\text{abs},w}$ should be as small as possible, and the fraction absorbed by the counter itself $f_{\text{abs},c}$ as large as possible. The absorption efficiency E_{abs} , expressed as a fraction, is given by $(1 - f_{\text{abs},w})(f_{\text{abs},c})$. The detection efficiency E_{det} is simply $(1 - f_{\text{losses}})$, where f_{losses} represents the fractional counting losses described above. The overall efficiency is then

$$E = E_{\text{abs}}E_{\text{det}} = [(1 - f_{\text{abs},w})(f_{\text{abs},c})][1 - f_{\text{losses}}]. \quad (7-1)$$

As previously mentioned E_{det} is essentially 100 percent for most counters used in diffractometry. Therefore E is determined by E_{abs} , which can be calculated from the dimensions and absorption coefficients of the window and counter, and Fig. 7-12 shows the result. Note particularly the dependence of E_{abs} on wavelength, due to the dependence of absorption coefficients on wavelength. The efficiency of any counter is low for very short wavelengths, because most of these hard x-rays pass right through window and counter and are absorbed by neither; at long wavelengths E_{abs} decreases because of increasing absorption of soft x-rays by the window.

Energy Resolution

In most counters the size of the voltage pulse produced by the counter is proportional to the energy of the x-ray quantum absorbed. Thus, if absorption of a Cu $K\alpha$ quantum ($\lambda = 1.54 \text{ \AA}$, $h\nu = 9 \text{ keV}$) produces a pulse of V volts, then absorption of a Mo $K\alpha$ quantum ($\lambda = 0.71 \text{ \AA}$, $h\nu = 20 \text{ keV}$) will produce a pulse of $(20/9)V = 2.2 V$.

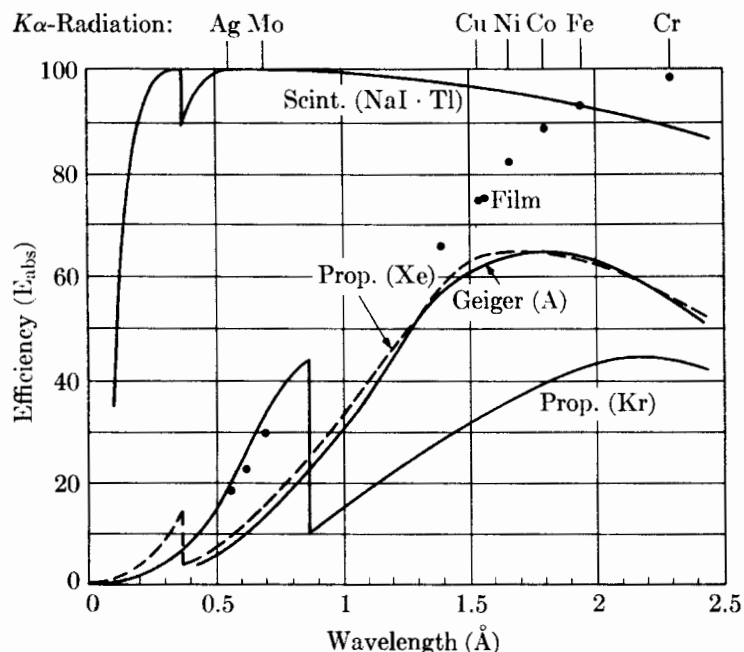


Fig. 7-12 Calculated values of absorption efficiency E_{abs} (in percent) of various kinds of counters and of photographic x-ray film (black dots). Parrish [7.8].

However, the size of a pulse is not sharply defined, even when the incident radiation is strictly monochromatic or, in energy terms, “monoenergetic.” Instead of all pulses having exactly the same size V as suggested, for example, by Fig. 7-9, they have sizes distributed around V roughly as indicated in Fig. 7-13. Here the ordinate, “counting rate,” is equivalent to the number of pulses having a particular size, so that this curve is a pulse-size distribution curve. If the width of the curve at half its maximum height is W and if V is the mean pulse size, then the resolution R of the counter is

$$R = \frac{W}{V} . \quad (7-2)$$

The smaller R , the better the resolution.

We will now examine the operation and performance of various counters.

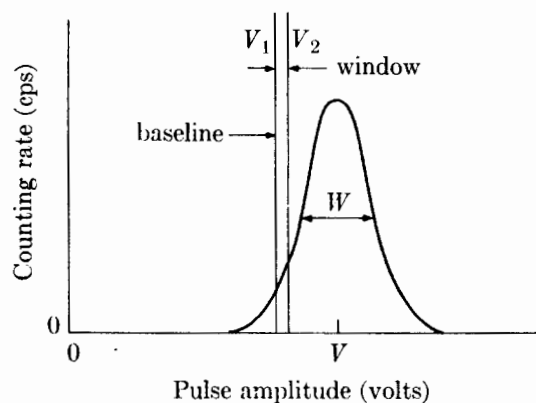


Fig. 7-13 Distribution curve of pulse size. (The “window” and “baseline” are explained in Sec. 7-9.)

7-5 PROPORTIONAL COUNTERS

Consider the device shown in Fig. 7-14, consisting of a cylindrical metal shell (the cathode), about 10 cm long and 2 cm in diameter, filled with a gas and containing a fine metal wire (the anode) running along its axis. Suppose there is a constant potential difference of about 200 volts between anode and cathode. One end of the cylinder is covered with a window of high transparency to x-rays. Of the x-rays which enter the cylinder, a small fraction passes right through, but the larger part is absorbed by the gas, and this absorption is accompanied by the ejection of photoelectrons and Compton recoil electrons from the atoms of the gas. The net result is ionization of the gas, producing electrons, which move under the influence of the electric field toward the wire anode, and positive gas ions, which move toward the cathode shell. At a potential difference of about 200 volts, all these electrons and ions will be collected on the electrodes, and, if the x-ray intensity is constant, there will be a small constant current of the order of 10^{-12} amp or less through the resistance R_1 . This current is a measure of the x-ray intensity. When operated in this manner, this device is called an *ionization chamber*. It was used in the original Bragg spectrometer but is now obsolete for the measurement of diffracted x-rays because of its low sensitivity. It is still used in some radiation survey meters.

The same instrument, however, can be made to act as a *proportional counter* if the voltage is raised to the neighborhood of 1000 volts. A new phenomenon now occurs, namely, multiple ionization or "gas amplification." The electric-field intensity is now so high that the electrons produced by the primary ionization are rapidly accelerated toward the wire anode and at an ever-increasing rate of acceleration, since the field intensity increases as the wire is approached. The electrons thus acquire enough energy to knock electrons out of other gas atoms, and these in turn cause further ionization and so on, until the number of atoms ionized by the absorption of a single x-ray quantum is some 10^3 to 10^5 times as large as the number ionized in an ionization chamber. As a result of this amplification a veritable avalanche of electrons hits the wire and causes an easily detectable pulse of current in the external circuit. This pulse leaks away through

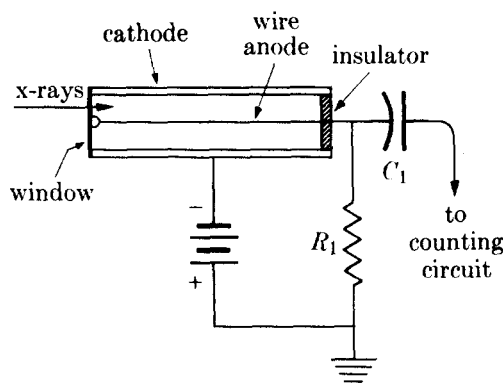


Fig. 7-14 Gas counter (proportional or Geiger) and basic circuit connections.

the large resistance R_1 but not before the charge momentarily added to the capacitor C_1 has been detected by the ratemeter or scaling circuit connected to C_1 . At the same time the positive gas ions move to the cathode but at a much lower rate because of their larger mass. This whole process, which is extremely fast, is triggered by the absorption of one x-ray quantum.

We can define a gas amplification factor A as follows: if n is the number of atoms ionized by one x-ray quantum, then An is the total number ionized by the cumulative process described above. (For example, if the gas in the counter is argon, energy of about 26 eV is required to produce an ion pair, i.e., a positive ion and an electron. If the incident radiation is Cu $K\alpha$ of energy 8040 eV, then the number n of ion pairs formed is $8040/26$ or 310.) Figure 7-15 shows schematically how the gas amplification factor varies with the applied voltage. At the voltages used in ionization chambers, $A = 1$; i.e., there is no gas amplification, since the electrons produced by the primary ionization do not acquire enough energy to ionize other atoms. But when the voltage is raised into the proportional counter region, A becomes of the order of 10^3 to 10^5 , and a pulse of the order of a few millivolts is produced. Moreover, the size of this pulse is proportional to the energy of the x-ray quantum absorbed, which accounts for the name of this counter. This proportionality is important, because it allows us to distinguish (Sec. 7-9) between x-ray quanta of different energies (wavelengths). (Historically, this counter was the first kind to exhibit such proportionality. There are now others.) Pulses from the counter go to a preamplifier, mounted immediately adjacent to the counter; here they are amplified enough to be transmitted, without too much attenuation, along several feet of cable to the main amplifier and the rest of the electronics.

The correct voltage at which to operate the counter is found as follows. Position the counter to receive an x-ray beam of constant intensity. Measure the

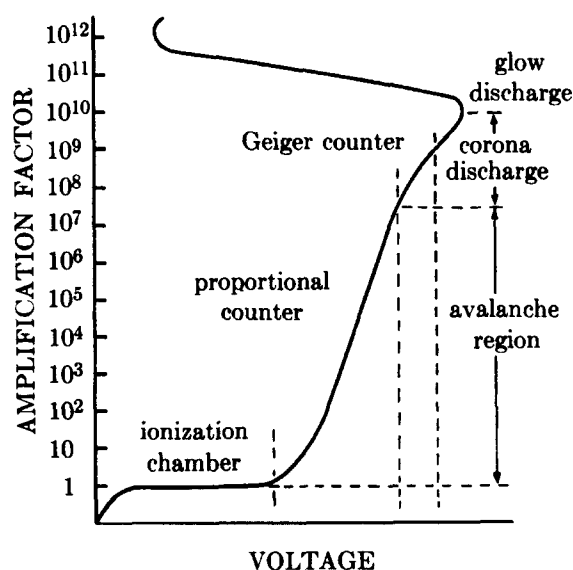


Fig. 7-15 Effect of voltage on the gas amplification factor. Friedman [7.9].

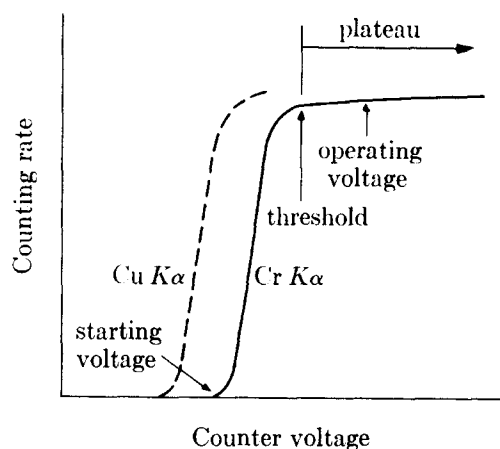


Fig. 7-16 Effect of voltage applied to proportional counter on observed counting rate at constant x-ray intensity (schematic).

counting rate with a ratemeter or scaler while slowly increasing the voltage applied to the counter from a low value. Figure 7-16 shows how the counting rate will vary with voltage. Below the starting voltage the pulse size is less than the input sensitivity of the counting circuit and no counts are observed. The pulse size and observed counting rate then increase rapidly with voltage up to the threshold of the plateau, where the counting rate is almost independent of voltage. The voltage is then fixed at about 100 volts above threshold. (Note that x-rays of longer wavelength require a higher counter voltage. This means that the counter voltage should be reset when the x-ray tube in the diffractometer is changed for one with a different target.)

The proportional counter is essentially a very fast counter and has a linear counting curve up to about 10,000 cps. This ability to separate closely spaced pulses is due to the fact that the avalanche triggered by the absorption of an x-ray quantum is confined to an extremely narrow region of the counter, 0.1 mm or less, and does not spread along the counter tube (Fig. 7-17). The rest of the counter volume is still sensitive to incoming x-rays.

The electric field near the end of the anode wire is not uniform. Most proportional counters are now made with a side window, rather than the end window shown in Fig. 7-17, so that x-ray absorption can take place in a region of uniform field.

The gas in the counter is usually xenon, argon, or krypton at a pressure somewhat less than atmospheric. Figure 7-12 shows that a krypton counter has about the same sensitivity for all the characteristic radiations normally used in diffraction. But an argon or xenon counter is much less sensitive to short wavelengths, an advantage in most cases. Thus, if a diffraction pattern is made with filtered radiation from a copper target, use of an argon counter will produce semi-monochromatic conditions, in that the counter will be highly sensitive to $\text{Cu } K\alpha$ radiation and relatively insensitive to the short wavelength radiation that forms the most intense part of the continuous spectrum. The diffraction background will therefore be lower than if a krypton counter had been used. (The

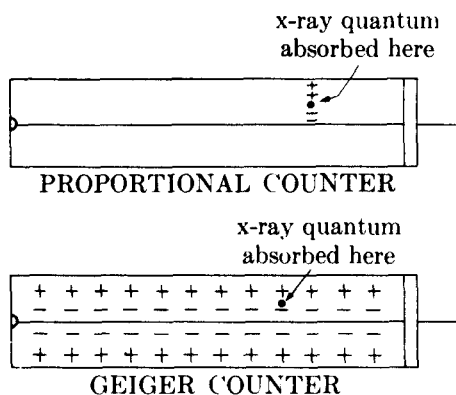


Fig. 7-17 Differences in the extent of ionization between proportional and Geiger counters. Each plus (or minus) symbol represents a large number of positive ions (or electrons).

student may wish to record the spectrum of the copper-target x-ray tube in a diffractometer. This can be done by operating it as a spectrometer, with a single crystal, such as quartz or rock salt, in the specimen holder and continuous scanning with a ratemeter and strip-chart recorder. With an argon-filled counter, the resulting spectrum will not look at all like what is expected (Fig. 1-5). Instead, only the $\text{Cu } K\alpha$ and $\text{Cu } K\beta$ lines will be visible on the chart, because the counter is insensitive to short wavelengths. The continuous spectrum can be observed only by effecting an opposite distortion: put several thicknesses of aluminum foil in the diffracted beam so as to absorb the $\text{Cu } K$ lines more than the short wavelengths; at the same time, expand the ratemeter scale to allow for the decreased intensity of all wavelengths. With sufficiently heavy filtration by aluminum, the spectrum can be so distorted that the maximum in the continuous spectrum will be more intense, as recorded, than the characteristic lines. It is an instructive experiment.)

In x-ray spectroscopy (Chap. 15), but not in diffraction, there is a need to measure soft x-rays of wavelength about 5–20 Å. Because ordinary windows would almost totally absorb such radiation, thin sheet plastic is used as a window, so thin that it leaks. To allow for this, a stream of counter gas is continuously passed through the counter, which is then called a *gas-flow proportional counter* [G.29, 7-10].

Another special type, the *position-sensitive proportional counter* [7.11, 12, 13] may become important for certain applications. The diffracted x-ray beam enters the counter through a side window, striking the anode wire, which lies in the plane of the diffractometer circle, approximately at right angles. Because the electron avalanche is sharply localized (Fig. 7-17), the point where the electrons hit the wire can be determined by electronically measuring the time required for the pulse to travel from the point of impact to the end of the wire. Thus the angular position 2θ of a diffracted beam is found, not in the usual way by moving a counter with a narrow entrance slit to the position of the beam (Fig. 7-1), but by finding where the beam strikes the wire of a *fixed*, wide-window counter. The counting circuit must include a multichannel analyzer (Sec. 7-9) in order to determine the profile of the diffraction line. This new method is applicable only over a restricted range of 2θ values, but such a range is all that need be examined in some problems.

7-6 GEIGER COUNTERS

If the voltage on a proportional counter is increased to the neighborhood of 1500 volts, it will act as a Geiger counter. Historically, this was the first electronic counter; it is also called a Geiger-Müller or G-M counter.

The applied voltage is now so high that not only are some atoms ionized but others are raised to excited states and caused to emit ultraviolet radiation. These ultraviolet photons travel throughout the counter at high speed (light travels 10 cm in a third of a nanosecond), knocking electrons out of other gas atoms and out of the cathode shell. All the electrons so produced trigger other avalanches, and the net result is that one tremendous avalanche of electrons hits the whole length of the anode wire whenever an x-ray quantum is absorbed anywhere in the tube (Fig. 7-17). As a result the gas amplification factor A is now much larger, about 10^8 to 10^9 , than in a proportional counter, and so is the size of the pulse produced, now some 1 to 10 volts. This means that no preamplifier is needed at the counter. On the debit side, all pulses have the same size, whatever the energy of the x-ray quanta.

The Geiger counter is also slow. Any one avalanche of electrons hits the anode wire in less than a microsecond, but the slowly moving positive ions require about 200 microseconds to reach the cathode. Thus the electron avalanche leaves behind it a cylindrical sheath of positive ions around the anode wire. The presence of this ion sheath reduces the electric field between it and the wire below the threshold value necessary to produce a Geiger pulse. Until this ion sheath has moved far enough away from the wire, the counter is insensitive to entering x-ray quanta. If these quanta are arriving at a very rapid rate, it follows that not every one will cause a separate pulse and the counter will become "choked." The resolving time is only about 10^{-4} sec, so that counting losses begin at a few hundred cps. Even the multichamber counter is not much better (Fig. 7-10); this counter has a number of chambers side by side, each with its own anode wire, and one chamber can therefore register a count while another one is in its insensitive period.

Because it cannot count at high rates without losses, the Geiger counter is now obsolete in diffractometry. It is still used in some radiation survey meters.

7-7 SCINTILLATION COUNTERS

This type of counter exploits the ability of x-rays to cause certain substances to fluoresce visible light, as in the fluorescent screens mentioned in Sec. 1-8. The amount of light emitted is proportional to the x-ray intensity and can be measured by means of a phototube. Since the amount of light emitted is small, a special kind of phototube called a *photomultiplier* has to be used in order to obtain a measurable current output.

The substance generally used to detect x-rays is a sodium iodide crystal activated with a small amount of thallium. It emits violet light under x-ray bombardment. (The details of this emission are roughly as follows. Absorbed x-rays ionize some atoms, i.e., raise some electrons from the valence to the

conduction band of NaI. These electrons then transfer some of their energy to the TI^+ ion. When the excited ion returns to its ground state, light is emitted.) The light-emitting crystal is cemented to the face of a photomultiplier tube, as indicated in Fig. 7-18, and shielded from external light by means of aluminum foil. A flash of light (scintillation) is produced in the crystal for every x-ray quantum absorbed, and this light passes into the photomultiplier tube and ejects a number of electrons from the photocathode, which is a photosensitive material generally made of a cesium-antimony intermetallic compound. (For simplicity, only one of these electrons is shown in Fig. 7-18.) The emitted electrons are then drawn to the first of several metal *dynodes*, each maintained at a potential about 100 volts more positive than the preceding one, the last one being connected to the measuring circuit. On reaching the first dynode, each electron from the photocathode knocks two electrons, say, out of the metal surface, as indicated in the drawing. These are drawn to the second dynode where each knocks out two more electrons and so on. Actually, the gain at each dynode may be 4 or 5 and there are usually at least 10 dynodes. If the gain per dynode is 5 and there are 10 dynodes, then the multiplication factor is $5^{10} = 10^7$. Thus the absorption of one x-ray quantum in the crystal results in the collection of a very large number of electrons at the final dynode, producing a pulse about as large as a Geiger pulse, i.e., of the order of volts. Furthermore, the whole process requires less than a microsecond, so that a scintillation counter can operate at rates as high as 10^5 counts per second without losses. The correct counter voltage is found by the method used for the proportional counter, by plotting counting rate vs. voltage (Fig. 7-16).

As in the proportional counter, the pulses produced in a scintillation counter have sizes proportional to the energy of the x-ray quanta absorbed. But the pulse size corresponding to a certain quantum energy is much less sharply defined, as shown in Fig. 7-19 for typical proportional and scintillation (NaI · TI) counters. As a result, it is more difficult to discriminate, with a scintillation counter, between x-ray quanta of different wavelengths (energies) on the basis of pulse size.

The efficiency of a scintillation counter approaches 100 percent over the usual range of wavelengths (Fig. 7-12), because virtually all incident quanta are absorbed, even in a relatively thin crystal.

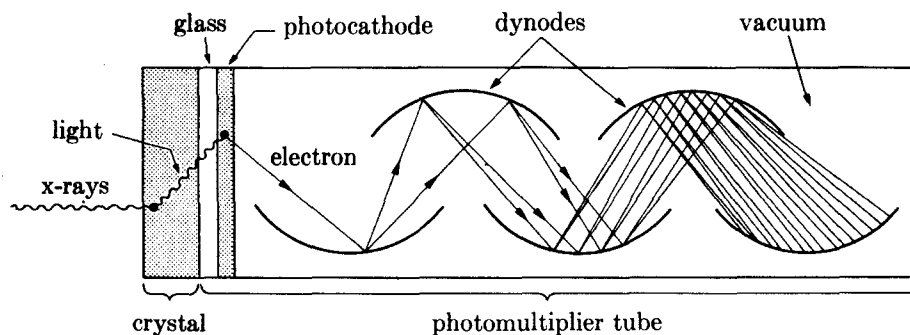


Fig. 7-18 Scintillation counter (schematic). Electrical connections not shown.

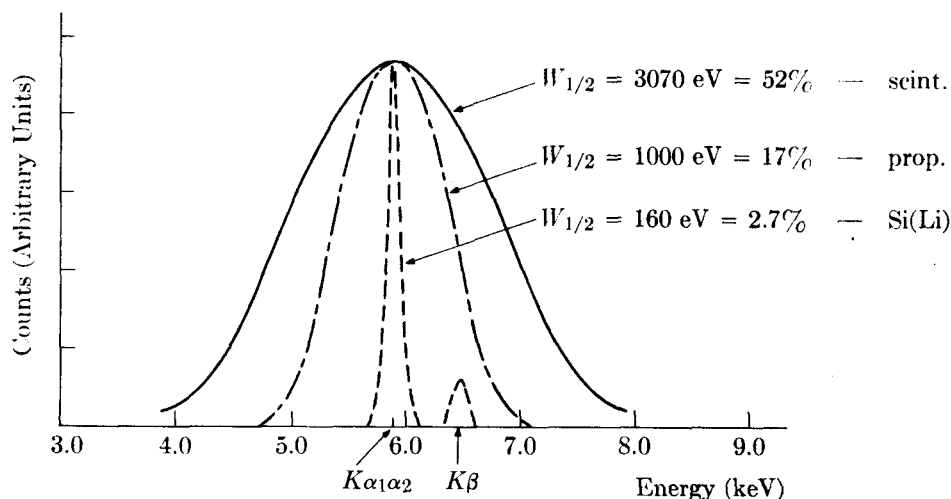


Fig. 7-19 Pulse-height distribution curves for three kinds of counter. Incident radiation is Mn $K\alpha$ ($\lambda = 2.10 \text{ \AA}$, $h\nu = 5.90 \text{ keV}$) and Mn $K\beta$ ($\lambda = 1.91 \text{ \AA}$, $h\nu = 6.50 \text{ keV}$). Frankel and Aitken [7.14].

7-8 SEMICONDUCTOR COUNTERS

Developed in the 1960s, semiconductors are the newest form of counter. They produce pulses proportional to the absorbed x-ray energy with better energy resolution than any other counter; this characteristic has made them of great importance in spectroscopy (Chap. 15). Although they have had little application in diffraction, it is convenient to describe them here along with the other counters.

Both silicon and germanium are used, germanium as a detector for gamma rays, because it is heavier and therefore a better absorber, and silicon for x-rays. Both contain a small amount of lithium, and they are designated Si(Li) and Ge(Li), inevitably referred to as “silly” and “jelly.” Their properties have been reviewed by Dearnaley and Northrop [7.15], Heath [7.16], and Gedcke [7.17], among others, and in an ASTM symposium [7.18].

Pure silicon is an intrinsic semiconductor. It has very high electrical resistivity, especially at low temperatures, because few electrons are thermally excited across the energy gap into the conduction band. However, incident x-rays can cause excitation and thereby create a free electron in the conduction band and a free hole in the valence band. As shown later, the absorption of one x-ray quantum creates about a thousand electron-hole pairs. If a high voltage is maintained across opposite faces of the silicon crystal, the electrons and holes will be swept to these faces, creating a small pulse in the external circuit.

It is essential that the silicon be intrinsic (*i*). It must neither be *n*-type, containing free electrons from donor impurities, nor *p*-type, containing free holes from acceptor impurities; in either type, the free charge carriers, at their usual concentrations, would overwhelm the few carriers produced by x-rays. Production of a reasonably large intrinsic crystal, which is not easy, requires two operations:

1. The starting material is a cylindrical crystal, some 3–5 mm thick and 5–15 mm

in diameter. It is p -type, having been lightly doped with boron. Lithium is applied to one face and diffused into the crystal at an elevated temperature, producing a gradient of lithium concentration from high to low through the thickness. The lithium exists as Li^+ ions, and the free electrons it provides convert the crystal into n -type on one side, where the lithium concentration is high, leaving the other side p -type.

2. A voltage is then applied, also at an elevated temperature, to opposite faces, positive on the n side and negative on the p side (called "reverse bias"). This causes the Li^+ ions to "drift" toward the p side, resulting in a wide central region of constant lithium concentration; this region is now intrinsic because it has equal lithium and boron concentrations.

The result is the lithium-drifted silicon counter sketched in Fig. 7-20. The crystal is virtually all intrinsic, with the p and n portions confined to thin surface layers, which are exaggerated in the drawing. The very small pulses from the counter are amplified to the millivolt level by a field-effect transistor, abbreviated FET. (There is no charge amplification, such as occurs in a gas counter. The pulse from the counter contains only the charge liberated by the absorbed x-rays.)

Putting aside all of the above details of semiconductor physics, we can regard a Si(Li) counter simply as a solid-state ionization chamber, with one difference. X-rays incident on a gas ionization chamber produce a *constant* current (Sec. 7-5). In a Si(Li) counter the current flows in discrete *pulses*, because the voltage is high enough to sweep the counter free of charge carriers (the electrons and holes are highly mobile) before the next incident photon creates new carriers.

A major disadvantage of the Si(Li) counter is that it must be operated at the temperature of liquid nitrogen ($77^\circ\text{K} = -196^\circ\text{C}$) in order to minimize (1) a constant current through the detector, even in the absence of x-rays, due to thermal excitation of electrons in the intrinsic region, and (2) thermal diffusion of lithium, which would destroy the even distribution attained by drifting. Even when not

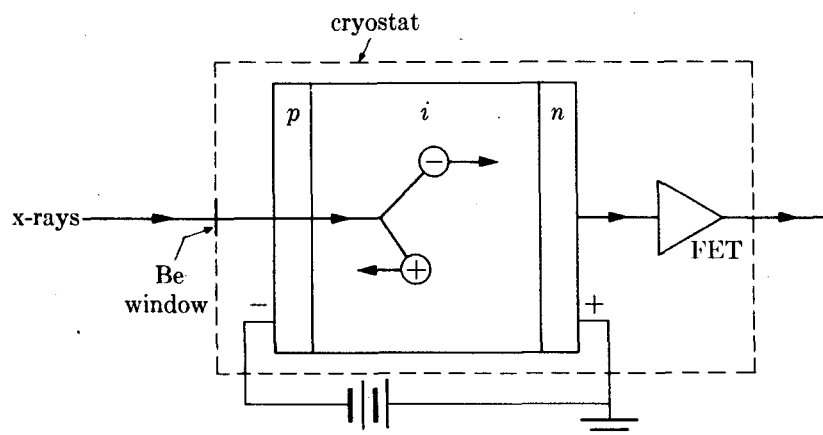


Fig. 7-20 Si(Li) counter and FET preamplifier, very schematic. Both are in a cooled evacuated space, and x-rays enter through a beryllium window. The counter is operated at about 1000 volts. \ominus = electron, \oplus = hole.

operating, the counter should not be allowed to warm too often to room temperature. Electronic "noise" in the FET increases with temperature and degrades the resolution. Thus both the counter and the FET have to be cooled, necessitating a bulky cryostat to hold several liters of liquid nitrogen (Fig. 15-10).

The efficiency of a Si(Li) counter resembles that of the other solid-state counter (scintillation), very high for intermediate wavelengths (Fig. 7-12). Very long wavelengths are partially absorbed by the counter window before they can reach the sensitive intrinsic layer. Very short wavelengths are partially transmitted by the entire counter.

The counting rate varies linearly with x-ray intensity up to rates of about 5,000-10,000 cps. Counting losses in the counter-electronics system occur in the electronics rather than the counter. The electronics are more complex than usual and include, besides the usual pulse amplifiers and shapers, a multichannel pulse-height analyzer (Sec. 7-9).

The excellent energy resolution of a Si(Li) counter is shown in Fig. 7-19. The width W of the pulse distribution is so small that the Si(Li) counter can resolve the $K\alpha$ and $K\beta$ lines of manganese, which the other two counters cannot do. Put another way, the resolution $R = W/V$ of the Si(Li) counter is 2.7 percent or some six times better than that of the proportional counter. For any kind of counter, both W and W/V vary with V , i.e., with the energy $h\nu$ of the incident x-rays. Therefore any description of counter performance must specify the x-ray energy at which it is measured; the 5.90 keV energy of the Mn $K\alpha$ line is the usual standard reference. The width W , incidentally, is often written as FWHM (full width at half maximum) in the literature of this subject.

To create an electron-hole pair in silicon at 77°K requires an average energy of 3.8 eV. The absorption of a Mn $K\alpha$ quantum should therefore create $5900/3.8 = 1550$ pairs. However, the actual number created by successive quanta might be 1540, 1560, 1555, ..., leading to a corresponding variation in the size of the output pulse. This statistical variation in the number of charge carriers created by x-ray absorption is the basic reason for the finite width W of the pulse distribution, and the same is true of proportional and scintillation counters. In the Si(Li)-FET counter, there is an even larger contribution to W , namely, electronic noise in the FET preamplifier. At the energy of Mn $K\alpha$ more than half of the observed value of W is due to noise in the FET. Beyond a certain counting rate, the resolution of the system worsens (W becomes larger) as the count rate increases.

As stated earlier, silicon counters are usually preferred for x-rays and germanium counters for the more energetic, shorter wavelength gamma rays of interest to nuclear physicists. This situation may change. Germanium counters are usable over the energy range of about 3-100 keV (4-0.1 Å), and *intrinsic* germanium crystals are now being made that do not require lithium drifting. They may find application in x-ray spectroscopy for wavelengths less than 4 Å.

In any counter except the Geiger, the average number n of ion pairs or electron-hole pairs produced is proportional to the energy E of the absorbed quantum. The actual

number has a Gaussian (normal) distribution about the mean, and the width at half maximum of this distribution is proportional to the standard deviation σ , which is equal to \sqrt{n} . Therefore the resolution R is

$$R = \frac{W}{V} = \frac{k_1 \sqrt{n}}{k_2 n} = \frac{k_3}{\sqrt{n}}, \quad (7-3)$$

where the k s are constants. The superior resolution of a Si(Li) counter is simply due to the large value of n , which is 1550 for Mn $K\alpha$. By comparison, n is only $5600/26 = 230$ for an argon proportional counter and the same radiation, because 26 eV are needed to create an ion pair in argon. Actually, the inherent resolution of a Si(Li) counter (the resolution in the absence of preamplifier noise) is even better, for complex reasons, than the above statistical argument suggests.

Because n is proportional to E , we can find from Eq. (7-3) the energy or wavelength dependence of the resolution:

$$R = \frac{k_3}{\sqrt{n}} = \frac{k_4}{\sqrt{E}} = \frac{k_4}{\sqrt{h\nu}} = k_5 \sqrt{\lambda}. \quad (7-4)$$

Although Eqs. (7-3) and (7-4) are useful for rough qualitative arguments, they do not include the substantial effect of electronic noise in Si(Li)-FET counters. A better estimate of resolution in such counters is given by

$$R = \frac{W}{V} = \frac{[(100)^2 + 2.62E]^{1/2}}{E}, \quad (7-5)$$

where E is the x-ray energy in eV and the term 100 eV in the numerator is the present level of the electronic noise. This relation is important in spectroscopy.

7-9 PULSE-HEIGHT ANALYSIS

All the counters in use today (proportional, scintillation, and semiconductor) are "proportional" in the sense that they produce pulses having a size (amplitude) that is proportional to the energy of the incident x-rays. Electrical circuits that can distinguish between pulses of different size can therefore distinguish between x-rays of different energies (wavelengths), and this ability is of great value in many experimental techniques. These circuits, in order of increasing complexity, are:

1. Pulse-height discriminator.
2. Single-channel pulse-height analyzer.
3. Multichannel pulse-height analyzer.

Circuits (1) and (2) may be used with ordinary diffractometers to increase the peak/background ratio of diffraction lines. They are by no means necessary; quite adequate diffraction patterns can be obtained from a wide variety of specimens with no other "discriminator" than a $K\beta$ filter. Circuit (3) is required only in x-ray spectroscopy (Chap. 15), in a very special kind of diffractometry (Sec. 7-10), and with a position-sensitive proportional counter. Any one of these circuits is more effective, the better the resolution of the counter with which it operates.

Pulse-Height Discriminator

Suppose that x-rays of three wavelengths $a > b > c$ are incident on a counter. Then the counter will produce pulses A, B, C of different size, C being the largest (Fig. 7-21). If a circuit is inserted, just ahead of the scaler or ratemeter, that will allow only pulses larger than a certain selected size (V_1 volts) to pass and discriminate against smaller ones, then the A pulses will not be counted and the system will be blind to wavelength a . Such a circuit is called a pulse-height discriminator. It may be of some value in decreasing diffractometer background due to the specimen's fluorescent radiation, when that radiation has a wavelength much longer than that which forms the diffraction lines, but it cannot weaken the short-wavelength components of the continuous spectrum.

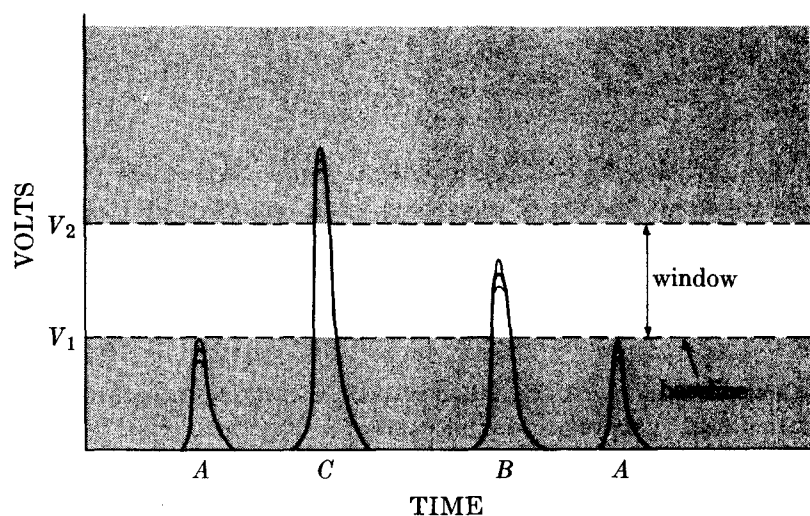


Fig. 7-21 Pulse-height discrimination and analysis. The statistical spread in pulse size, measured by the width W of Fig. 7-13, is suggested above by the variable heights of each pulse.

Single-Channel Pulse-Height Analyzer

This instrument discriminates against any pulses smaller than V_1 volts (Fig. 7-21). In addition, it contains an *anti-coincidence circuit* that rejects any pulse larger than V_2 , because such a pulse will simultaneously trigger both the V_1 and V_2 levels. The net result is that only pulses having sizes between V_1 and V_2 volts are passed. Out of the mixture of A , B , and C pulses entering the analyzer, only B pulses are passed to the counting circuit. The level V_1 is called the *baseline*, and the range from V_1 to V_2 is the *window* or *channel*. (Here, then, is another sense of the word "window." It is not a physical window, as at the entrance to a counter, but a voltage window.)

Both V_1 and V_2 are adjustable. If the window ($V_2 - V_1$) is made quite small, say 0.5 volt, and the baseline V_1 continuously varied from low values to high values, with ($V_2 - V_1$) constant, then a narrow window can be traversed across the voltage range of pulse heights; if the counting rate is measured at each setting

of V_1 , the result is an analysis of the distribution of pulse heights. It is in this way that curves like that of Fig. 7-13 are measured.

An analyzer can markedly reduce the background of a diffraction pattern, chiefly by excluding short-wavelength white radiation. For example, examining the 111 line from silicon powder with copper radiation and a xenon-filled proportional counter, Parrish [7.8] found the peak/background ratio to be 57 without an analyzer and 146 with one. To achieve this almost three-fold improvement, the analyzer window was centered on the center V (Fig. 7-13) of the Cu $K\alpha$ distribution and made wide enough to accept about 90 percent of it.

This method works best when the wavelength to be passed and the wavelength to be rejected are far apart. If they are close together, or if the counter has poor resolution, it will be hard to pass one and reject the other. There will then be two pulse distributions like that of Fig. 7-13, side by side and partially overlapping. A window set to pass a reasonable proportion of one set of pulses will also pass some of the other set.

Problems of window settings can arise even when the incident x-rays are monochromatic, because pulses of *two* different sizes can be produced. This can occur when the incident radiation is energetic enough to cause x-ray fluorescence in the counter. The fluorescent radiation may escape from the counter without causing any ionization, carrying with it some of the energy that would normally be absorbed. An *escape peak* of smaller-than-normal pulses is then formed, corresponding to this less-than-normal energy absorption.

As a specific example, consider the absorption of Mo $K\alpha$ radiation ($\lambda = 0.71 \text{ \AA}$, energy $E_1 = 17.4 \text{ keV}$) in a krypton-filled proportional counter. The K absorption edge of krypton is at 0.87 \AA ($W_K = 14.3 \text{ keV}$), so that Mo $K\alpha$ radiation can cause the emission of Kr $K\alpha$ radiation ($\lambda = 0.98 \text{ \AA}$, energy $E_2 = 12.6 \text{ keV}$). Some of the Mo $K\alpha$ quanta are absorbed with a total loss of energy, causing normal pulses of average size $V_n = kE_1 = 17.4 k$ volts, where k is a constant. Absorption of other Mo $K\alpha$ quanta will involve an energy loss in the counter of only $(E_1 - E_2)$, because of the escaping Kr $K\alpha$, causing escape-peak pulses of average size $V_{ep} = k(E_1 - E_2) = k(17.4 - 12.6) = 4.8 k$ volts. These two processes are illustrated in Fig. 7-22(a), where k is evidently about 1.9. (The term *escape peak* may be misleading to some. We see from this example that the size of escape-peak pulses corresponds *not* to the escaping energy, but to the difference between the normal and escaping energies.) Shown in (b) are the normal and escape peaks for Cu $K\alpha$ radiation incident on a xenon counter; here the fluorescent radiation is the $L\alpha_1$ line.

The situation shown in Fig. 7-22(a) is unusual, in that there are more pulses in the escape peak than in the normal peak. If the window of a pulse-height analyzer is set to pass only the normal Mo $K\alpha$ pulses, then the observed counting rate (= observed x-ray intensity) would be less than half the value observed with no analyzer at all because without an analyzer all pulses would be counted. The number of pulses in the escape peak will be larger, relative to that in the normal peak, the greater the fluorescence yield (Sec. 1-5) of the counter material and the lower the absorption coefficient of the counter material for its own fluorescent radiation.

Escape pulses can occur in any "proportional" counter. In a NaI(Tl) scintillation

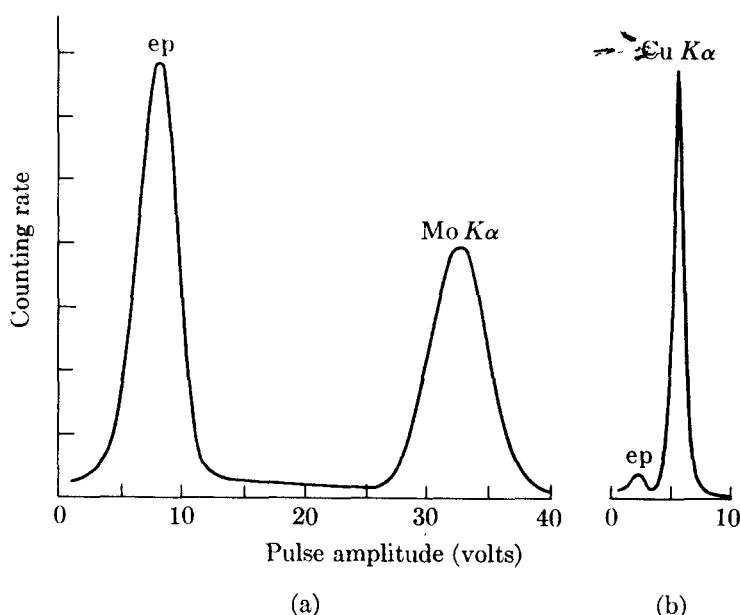


Fig. 7-22 Pulse-height distribution curves showing escape peaks (ep) in proportional counters for (a) Mo $K\alpha$ radiation incident on a krypton counter and (b) Cu $K\alpha$ radiation incident on a xenon counter. Parrish [7.8].

counter they are caused by fluorescent iodine K radiation; in a Si(Li) counter by fluorescent silicon K radiation.

Escape peaks can be troublesome in x-ray spectroscopy. When several wavelengths are incident on the counter, the escape peak for wavelength λ_1 may fall on or near the normal peak for wavelength λ_2 , causing uncertainty in the identification of λ_2 .

Multichannel Pulse-Height Analyzer

This remarkable instrument, called MCA for short, usually has not one but upward of a thousand channels. It is designed to separate pulses from a counter that is receiving incident radiation of many wavelengths, by sorting pulses according to their size (amplitude).

An MCA is actually a special-purpose computer with three functions [7.18]:

1. *Digitizing.* An analog-to-digital converter (ADC) converts the analog information contained in each pulse (amplitude in volts) into digital form, suitable for storage in a memory.

2. *Sorting and storage.* These operations are performed in the memory of the MCA. If the x-ray energy range to be examined extends from, say, 0 to 20 keV and the MCA has 1000 channels, then each channel spans an energy range of 20 eV. Channel number 295 would receive from the ADC information about any pulse activity in the range 5880–5900 eV. This channel would therefore get information (number of counts) about a vertical slice near the center of the Mn $K\alpha$ pulse distribution shown in Fig. 7-19; for the Si(Li) counter shown there, the base of the pulse distribution appears to be about 300 eV wide; information about Mn $K\alpha$ pulses would therefore be spread over 15 channels of the MCA.

3. *Display.* The contents of the MCA memory (total counts in each channel) may be displayed visually as counts vs. channel number (= counts vs. x-ray energy) on a TV screen or by an X-Y plotter, or they may be recorded on printed tape, punched tape, or magnetic tape.

The operation of multichannel and single-channel instruments in performing pulse-height analysis may be contrasted as follows. In a single-channel instrument the entire energy range is scanned serially in time by one moving channel, as suggested by Fig. 7-13. In the MCA, a large number of fixed channels covers the energy range and all channels simultaneously receive the count-rate information appropriate to each channel.

Applications of the MCA to specific problems are given in Chap. 15 and in the next section.

7-10 SPECIAL KINDS OF DIFFRACTOMETRY

The ability of the MCA to sort out signals of various magnitudes has permitted the development of new kinds of diffractometers, radically different from the conventional, moving-counter instrument to which this chapter is mainly devoted.

Energy-Dispersive Diffractometry

In the standard diffractometer, atomic planes of various spacings d in a powder specimen reflect a single wavelength in various directions 2θ ; the diffraction pattern is observed by moving a counter to the position of each diffracted beam in turn. On the other hand, if the incident beam consists of white radiation and the angle θ is fixed for all planes, the different sets of planes will reflect a set of different wavelengths into a counter set at a fixed position 2θ . If the counter is "proportional" and connected to a multichannel analyzer, the reflected wavelengths can be sorted out on the basis of their energies. This procedure, called *energy-dispersive diffractometry*, was first developed by Giessen and Gordon [7.19, 7.20] and Buras *et al.* [7.21] independently.

It is now appropriate to write the Bragg law in terms of quantum energy E rather than wavelength λ :

$$E = h\nu = \frac{hc}{\lambda} = \frac{hc}{2d \sin \theta}. \quad (7-6)$$

For E in keV and d in Å, this becomes (see Eq. 1-4)

$$E = \frac{6.20}{d \sin \theta}. \quad (7-7)$$

At constant θ , measurement of E will give the spacing d of each set of planes, and their indices (hkl) are found by the methods of Chap. 10. The experimental arrangement and an example of the results obtained, from a plot of the contents of the various channels of the MCA, are shown in Fig. 7-23. The specimen was a sheet of polycrystalline platinum.

The fluorescent L lines of platinum appear at the left of Fig. 7-23(b). The energies of these lines are independent of 2θ . The diffraction lines, on the other hand, have

energies that depend on 2θ according to Eq. (7-7). Therefore the whole diffraction pattern can be shifted to higher or lower energies by changing 2θ , if it is necessary to prevent an overlap of fluorescent and diffraction lines. (If the nature of the specimen is entirely unknown, the presence of the fluorescence lines can be advantageous. The fluorescence lines disclose the chemical elements present in the specimen, while the diffraction lines disclose its crystal structure. See Chaps. 14 and 15.)

Compared to the conventional method (single wavelength, moving counter), energy-dispersive diffractometry is much faster, because the diffraction pattern is acquired simultaneously rather than serially. Typically, the entire pattern can be recorded in 1 to 5 minutes, whereas the conventional technique requires over an hour. However, the resolution of closely spaced diffraction lines is inferior to that of the conventional technique. Also on the debit side are the added cost of an MCA and the inconvenience of cooling the Si (Li) counter.

Some specimens, notably steels, give diffraction patterns composed of rather widely separated lines. For such materials high resolution is not needed. Voskamp [7.22] has

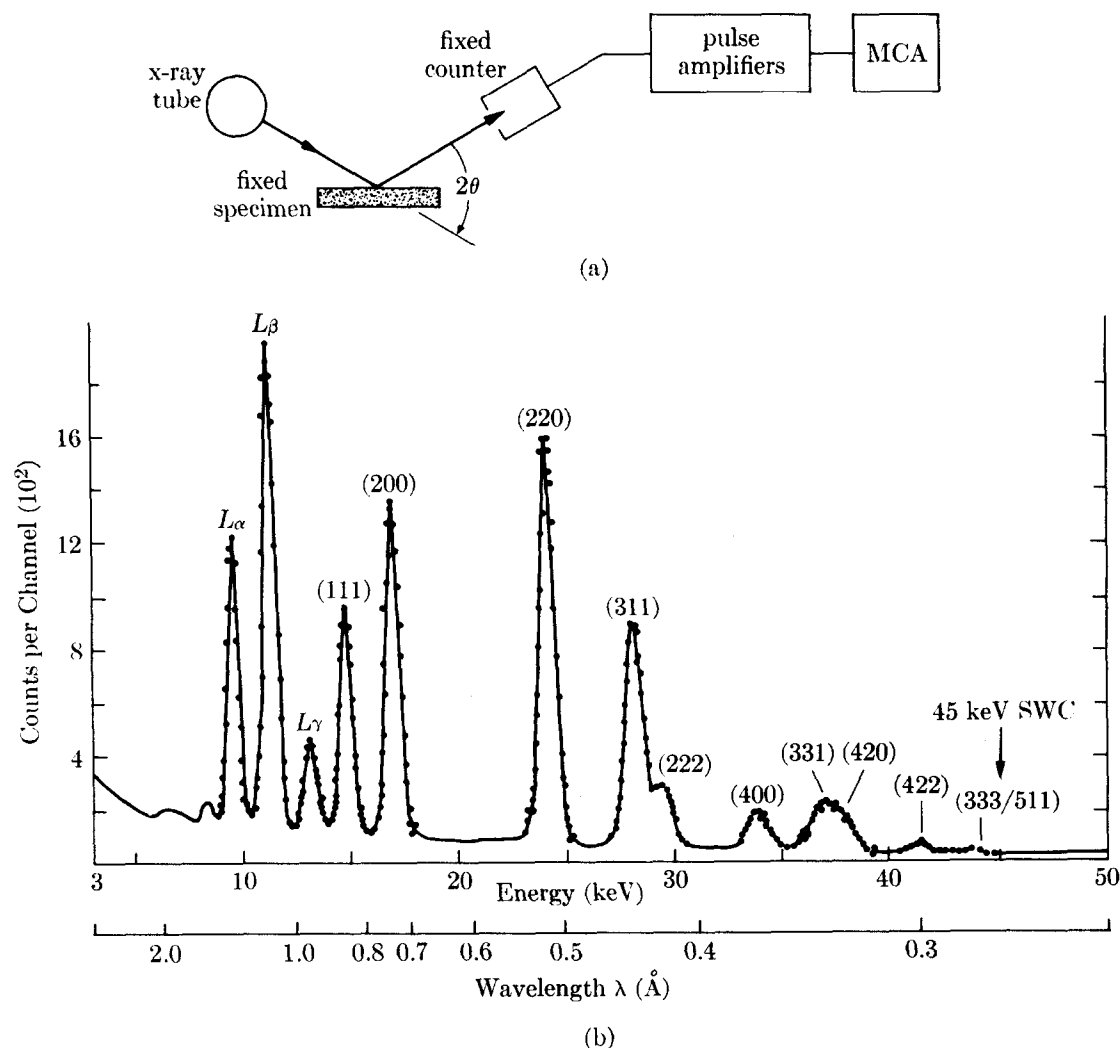


Fig. 7-23 Energy-dispersive diffractometry. (a) Experimental arrangement. The x-ray tube is seen end on. Diffracted-beam collimator not shown. (b) Diffraction pattern of polycrystalline platinum at $2\theta = 21.4^\circ$ obtained with a Si(Li) counter and an iron-target x-ray tube operated at 45 kV and 8 mA. SWC = short wave cutoff = short-wavelength limit of incident beam. Giessen and Gordon [7.20].

described the use of energy-dispersive diffractometry for the examination of steels and gives references to other applications.

Energy-dispersive diffractometry has not yet been widely used. Prophecy is always risky, but it may turn out that this method will be most useful in process control, such as chemical analysis (Chap. 14), because it is fast, involves no counter movement, and is easily adapted to automation.

Time-Analysis Diffractometry

This is a very recent development. It involves a side-window position-sensitive proportional counter (Sec. 7-5), a multichannel analyzer, and the measurement of the angular positions of many diffraction lines simultaneously. The anode wire of the counter, which is long and *curved*, coincides with a segment of the diffractometer circle and is connected, through appropriate circuits, to an MCA. The powder specimen is in the form of a thin rod centered on the diffractometer axis. The geometry of the apparatus therefore resembles that of a Debye-Scherrer camera (Fig. 6-2), except that the curved film strip is replaced by a curved counter.

When "monochromatic" radiation is incident on the specimen, it sends out diffracted beams at particular 2θ angles. These beams enter the side window of the counter at particular points, causing pulse formation at those points. The times required for these pulses to travel to the end of the counter are converted to digital form, analyzed, and sorted by the MCA. The contents of the MCA memory are therefore number of pulses (counts) as a function of the position on the anode wire where the pulses originated (angle 2θ). A display of the contents of the MCA resembles the pattern recorded by a conventional diffractometer (Fig. 7-5).

This method is fast, because all diffracted beams incident on the counter are measured simultaneously. However, the arc of the present counter subtends a 2θ angle of only 60° . Although the counter is fixed in position for any one measurement, it may be rotated around the diffractometer axis to cover any desired 2θ range, for example, 20° to 80° or 90° to 150° . If the whole pattern is to be examined from near 0° to near 180° , the measurement is made in three overlapping steps. The present instrument has 1000 channels, so that each channel represents $0.06^\circ 2\theta$.

This technique is still too new to have an agreed-on name, but perhaps "time-analysis diffractometry" is appropriate. The instrument itself has been aptly called an *electronic powder camera* by the manufacturer [7.23].

7-11 SCALERS

A scaler is an electronic device which counts each pulse produced by the counter. Once the number of pulses over a measured period of time is known, the average counting rate is obtained by simple division.

A scaler consists of a number of identical *stages* connected in series. Each stage is a circuit that divides, or scales down, the entering pulses by a constant factor before transmitting them to the next stage. This factor is 10 in a *decade scaler* and 2 in a *binary scaler*.

The first stage of a decade scaler transmits one pulse to the second stage for every ten pulses that enter the first stage. In a five-stage scaler the fifth stage will have transmitted one pulse when 10^5 pulses have entered the scaler, and the *scaling factor* is said to be 10^5 . If, say, 12,327 pulses have entered the scaler when

it is turned off, that count will be displayed as a decimal number on the front of the scaler, usually by ten-position glow tubes.

A binary scaler operates in a similar way, but now the scaling factor is 2^n , where n is the number of stages. Some binary scalers do not appear to be binary to the user, because the contents of the individual stages are not displayed; only the total count, in decimal form, appears at the front of the scaler.

A scaler can be operated in two ways to obtain the average counting rate:

1. *Counting for a fixed time.* The desired time t is selected by a switch, the START COUNT button is pushed, and the timer automatically stops the scaler after t seconds. The average counting rate is then N/t , where N is the displayed number of pulses (counts).

2. *Counting a fixed number of pulses.* The desired number of counts N is selected by a switch. If N is to be, say, 10,000 counts, the switch will connect the timer to the output of the fourth stage of a decade scaler. When 10,000 pulses have entered the scaler, the fourth stage will transmit its first pulse and that pulse will stop the timer.

Because the arrival of x-ray quanta in the counter is random in time, the accuracy of a counting rate measurement is governed by the laws of probability. Two counts of the same x-ray beam for identical periods of time will not be precisely the same because of the random spacing between pulses, even though the counter and scaler are functioning perfectly. Clearly, the accuracy of a rate measurement of this kind improves as the time of counting is prolonged, and it is therefore important to know how long to count in order to attain a specified degree of accuracy. The number of pulses N counted for a fixed time in repeated measurements of a constant x-ray intensity will have a Gaussian (normal) distribution about the true value N_t obtained by averaging many measurements, with a standard deviation σ of \sqrt{N} . The relative standard deviation to be expected in a single count of N pulses is then

$$\text{Relative } \sigma = \frac{\sqrt{N}}{N} (100) = \frac{100}{\sqrt{N}} \text{ percent.} \quad (7-8)$$

The probable error* in a single count is

$$\text{Probable error} = 0.67 (\text{relative } \sigma) = \frac{67}{\sqrt{N}} \text{ percent.} \quad (7-9)$$

* The probable error is that which is just as likely to be exceeded as not. Three times the probable error is a somewhat more useful figure, as the probability that this will be exceeded is only 0.04. Thus, if a single measurement gives 1000 counts, then the probable error is $67/\sqrt{1000} = 2.1$ percent or 21 counts. Then the probability is 0.5 that this count lies in the range $N_t \pm 21$, where N_t is the true number of counts, while the probability is 0.96 that the measured value lies in the range $N_t \pm 63$.

For some of the total counts obtainable from a decade scaler, these expressions give the following errors:

Number of pulses counted	Relative standard deviation (percent)	Probable error (percent)
1,000	3.2	2.1
10,000	1.0	0.7
100,000	0.3	0.2

Note that the error depends only on the number of pulses counted and not on their rate, which means that high rates and low rates can be measured with the same accuracy, if the counting times are chosen to produce the same total number of counts in each measurement. It also follows that the second scaling method outlined above, in which the time is measured for a fixed number of counts, is generally preferable to the first, since it permits intensity measurements of the same accuracy of both high- and low-intensity beams.

The probable error in the measured intensity of a diffraction line *above* background increases as the background intensity increases. If N_P and N_B are the numbers of counts obtained in the same time at the peak of the diffraction line and in the background adjacent to the line, respectively, then we are more interested in the error in $(N_P - N_B)$ than in the error in N_P . When two quantities are combined, the result has a variance equal to the sum of the variances of the quantities involved. (Variance = σ^2 , where σ = standard deviation.) In this case,

$$\begin{aligned}\sigma_{P-B}^2 &= \sigma_P^2 + \sigma_B^2 = N_P + N_B; \\ \sigma_{P-B} &= (N_P + N_B)^{1/2}; \\ \text{Relative } \sigma_{P-B} &= \frac{(N_P + N_B)^{1/2}}{(N_P - N_B)}.\end{aligned}\tag{7-10}$$

As indicated in Sec. 7-2, the integrated intensity of a diffraction line may be measured with a scaler by determining the average counting rate at several angular positions of the counter. The line profile, the curve of intensity vs. 2θ , is then plotted on graph paper, and the area under the curve, and above the continuous background, is measured with a planimeter. To obtain the same relative accuracy of both the line profile and the adjacent background, all measurements should be made by counting a fixed number of pulses.

A faster and more accurate method of measuring integrated intensity exploits the integrating property of the scaler. In Fig. 7-24 the shaded area P is the integrated intensity of the diffraction line shown. Select two counter positions $2\theta_1$ and $2\theta_2$, well into the background on either side of the line. Scan from $2\theta_1$ to $2\theta_2$, the scaler being started at the beginning of the scan and stopped at the end. Let the time required for this scan be t and the number of counts accumulated be N_{PB} ; this number is proportional to the sum of the areas P and B . Then count for a time $t/2$ at $2\theta_1$ and for a time $t/2$ at $2\theta_2$. Let the total count accumulated

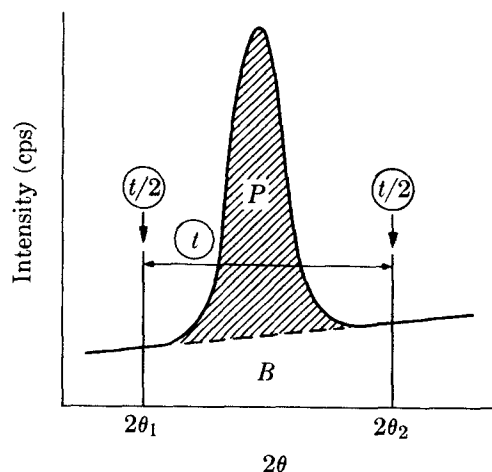


Fig. 7-24 Determination of integrated intensity by scanning and measuring counts with a scaler. The encircled symbols are the times spent in counting.

in these two fixed-position measurements be N_B . This number is proportional to the area B , because it is the count that would have been obtained in a scan for time t from $2\theta_1$ to $2\theta_2$ if the diffraction peak were absent. The integrated intensity of the peak is then

$$N_P = N_{PB} - N_B \quad (7-11)$$

When the integrated intensities of two diffraction lines are to be compared, both lines must be scanned with the same counter slit (receiving slit) at the same speed.

Because this method involves counting for a fixed time, the background and low-intensity portions of the diffraction line are measured with less accuracy than the high-intensity portions. The counting time should be chosen so that the low intensities are measured to the accuracy required by the particular problem involved; it will then follow that the high intensities are measured with unnecessarily high accuracy, but that is unavoidable in a fixed-time method.

7-12 RATEMETERS

The counting-rate meter, as its name implies, is a device which indicates the average counting rate directly without requiring, as in the scaler-timer combination, separate measurements of the number of counts and the time. It does this by a circuit which, in effect, smooths out the succession of randomly spaced pulses from the counter into a steady current, whose magnitude is proportional to the average rate of pulse production in the counter.

The heart of a ratemeter circuit is a series arrangement of a capacitor and resistor. To understand the action of a ratemeter, we must review some of the properties of such a circuit, notably the way in which the current and voltage vary with time. Consider the circuit shown in Fig. 7-25(a), in which the switch S can be used either to connect a to c and thus apply a voltage to the capacitor, or to connect b to c and thus short-circuit the capacitor and resistor. When a is suddenly connected to c , the voltage across the capacitor reaches its final value V not

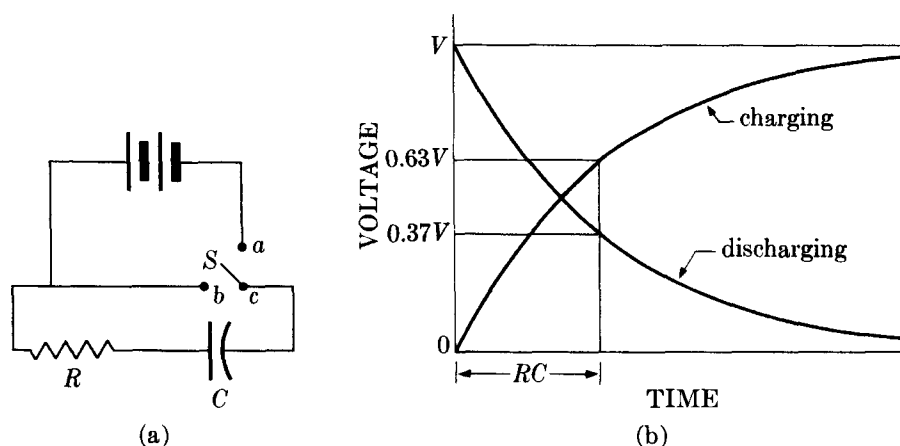


Fig. 7-25 The capacitor-resistor circuit.

instantaneously but only over a period of time, and at a rate which depends on the resistance R and the capacitance C , as shown in Fig. 7-25(b). The product of R and C has the dimensions of time (seconds, in fact, if R is in megohms and C in microfarads), and it may be shown that the voltage across the capacitor reaches 63 percent of its final value in a time given by RC , known as the *time constant* of the circuit. The time required to reach 99 percent of its final value is $4.6RC$. Conversely, if the fully charged capacitor, bearing a charge $Q = CV$, is suddenly shorted through the resistor by connecting b to c , the charge does not immediately disappear but leaks away at a rate dependent on the time constant. The charge drops to 37 percent of its initial value in a time equal to RC and to 1 percent in a time equal to $4.6RC$.

A complete ratemeter circuit consists of two parts. The first is a pulse-amplifying and pulse-shaping portion which electronically converts the counter pulses, which vary in amplitude and shape from counter to counter, into rectangular pulses of fixed dimensions in voltage and time. These pulses are then fed into the second portion, which is the measuring circuit shown in Fig. 7-26, a circuit basically similar to that of Fig. 7-25(a) and having a time constant R_2C_2 . S , shown as a simple switch, is actually an electronic circuit which connects a to c each time a pulse arrives and then connects b to c immediately afterwards. A constant charge

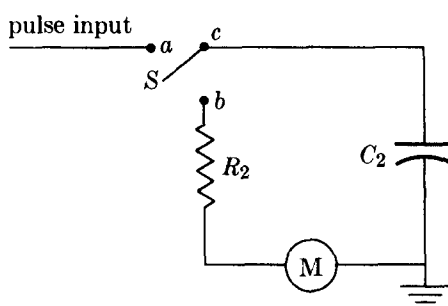


Fig. 7-26 Measuring portion of ratemeter circuit.

is thus added to the capacitor for each pulse received and this charge leaks away through the resistor until, at equilibrium, the rate of addition of charge is just balanced by the rate of leakage. The rate of charge leakage is simply the current through the microammeter M , which therefore indicates the rate of pulse production in the counter and, in turn, the x-ray intensity. The circuit usually contains, in addition to the indicating meter, a chart recorder which produces a continuous record of the intensity.

Even when the x-ray intensity is constant (constant average counting rate), the spacing of the counter pulses is random in time, which means that the counting rate actually varies with time over short periods. The ratemeter responds to these statistical fluctuations in the counting rate, and its response speed is greater the smaller the time constant. This follows from the discussion of the capacitor-resistor circuit: any change in the pulse rate causes a change in the current through the circuit, but the latter change always lags behind the former; the amount of lag is less for a small time constant than for a large one. Random fluctuations in the counting rate are therefore more evident with a small time constant, because the current in the circuit then follows the changes in counting rate more closely. This feature is illustrated in Fig. 7-27, which shows the automatically recorded output of a ratemeter when the counter is receiving a constant-intensity x-ray beam. The large fluctuations at the left have been reduced in magnitude by successive increases in the time constant, effected by changing the value of C_2 . Evidently, a *single* reading of the position of the indicating meter needle or the recorder pen of a ratemeter may be seriously in error, and more so at low time constants than at high. In Sec. 7-11 we saw that the error in a counting-rate measurement decreased as the number of counts increased. Now it may be shown that a ratemeter acts as if it counted for a time $2R_2C_2$, in the sense that the accuracy of any single reading is equivalent to a count made with a scaler for a time $2R_2C_2$. Therefore, the relative probable error in any single ratemeter reading is given by the counterpart of Eq. (7-9), namely by

$$\text{Probable error} = \frac{67}{\sqrt{2nR_2C_2}} \text{ percent}, \quad (7-12)$$

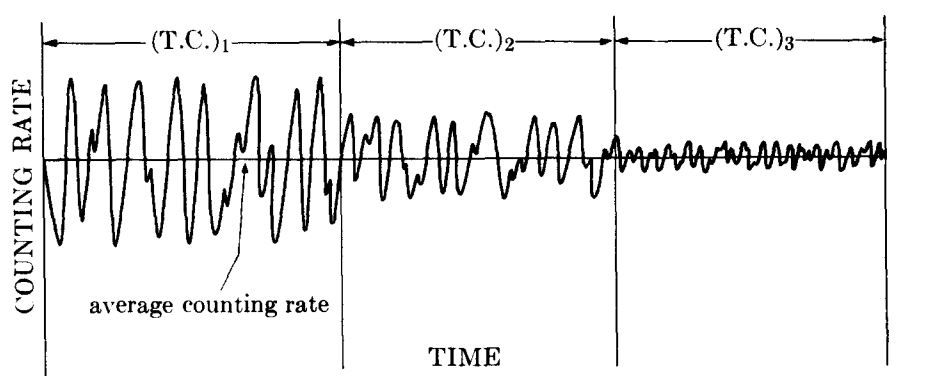


Fig. 7-27 Effect of time constant (T.C.) on recorded fluctuations in counting rate at constant x-ray intensity (schematic). Time constants changed abruptly at times shown. $(T.C.)_1 < (T.C.)_2 < (T.C.)_3$.

where n is the average counting rate. This equation also shows that the probable error is less for high counting rates than for low, when the time constant remains the same; this effect is evident on the chart recording of any diffraction line, where the pen fluctuations are smaller at the top of the line than in the background.

The most useful feature of a ratemeter is its ability to follow *changes* in the average counting rate, a function which the scaler is totally unable to perform, since a change in the average counting rate occurring during the time a count is being made with a scaler will go entirely undetected. It is this feature of a ratemeter which is so useful in diffractometry. A diffraction pattern can be scanned from one end to the other, and the moving counter automatically transmits, through the ratemeter, a continuous record of the intensity it observes as the diffraction angle is changed. On the other hand, the ratemeter is less accurate than the scaler, both because of the unavoidable statistical fluctuations in its output and because of the errors inherent in its indicating or recording instruments.

As mentioned earlier, a large time constant smooths out fluctuations in the average counting rate by increasing the response time to changes in rate. But when a sharp diffraction line is being scanned, the average counting rate is changing rapidly and we would like the ratemeter to indicate this change as accurately as possible. From this point of view a short response time, produced by a small time constant, is required. A ratemeter must therefore be designed with these two conflicting factors in mind, and the time constant should be chosen large enough to smooth out most of the statistical fluctuations and yet small enough to give a reasonably short response time.

Most commercial ratemeters have several scales available to cover various ranges of x-ray intensity (100, 1000, and 10,000 cps for full-scale deflection of the recorder pen, for example). Smaller time constants are used with the higher scales, just as short counting times are used with a scaler when the counting rate is high. In some instruments, the time constant appropriate to each scale is fixed by the manufacturer, and in others the operator can select any one of several time constants, ranging from about 0.5 to 15 sec, by switches which insert the proper capacitance in the circuit. The proper time constant to use is, of course, not unrelated to the scanning speed, for a fast scan demands a fast response from the ratemeter and therefore a short time constant. A time constant which is too large for the scanning speed used will slightly shift the peaks of diffraction lines in the direction of the scan and lower their maximum intensity and, because of its excessive smoothing action, may actually obliterate weak diffraction lines and cause them to go unnoticed. In choosing a time constant, it is therefore better to err on the short side. A good rule to follow is to make the time constant less than half the *time width* of the receiving slit, where the time width is defined as the time required for the slit to travel its own width. For example, if a 0.2° slit is used at a scanning speed of $2^\circ/\text{min}$, then the time width of the slit is $(0.2/2)(60) = 6$ sec, and the time constant should therefore be less than 3 sec. The same rule can be used to find the proper slit width for a given scanning speed when the time constant is fixed.

The relation between the x-ray intensity, i.e., the average counting rate, and the deflection of the recorder pen may usually be made linear or logarithmic, at

the turn of a switch. Logarithmic recording is useful when looking for weak lines or when exploring an unknown pattern; weak lines will be emphasized and the recording of strong lines will not go off-scale. If there is any doubt about the relation between x-ray intensity and pen deflection, it may be established experimentally by a procedure similar to that used for determining the counting rate at which losses begin, as outlined in Sec. 7-4. A number of identical metal foils are placed in a strong diffracted beam entering the counter and these are withdrawn one by one, with the counter in a fixed position. After each withdrawal, the counting rate is measured accurately with a scaler, and the ratemeter operated for a time at least equal to the scaling time, the recording chart speed being selected to give a trace of reasonable length. An average straight line is then drawn through each trace, in such a way as to make the positive and negative fluctuations as nearly equal as possible. Finally, the distances of these straight lines from the chart zero are plotted against the corresponding average counting rates as determined by the scaler, and the calibration curve so obtained is used as a basis for future intensity measurements with the ratemeter-recorder combination.

7-13 MONOCHROMATIC OPERATION

The background of a diffraction pattern obtained with a diffractometer may be reduced by means of a single-channel pulse-height analyzer, as mentioned in Sec. 7-9. An even better method is to use a crystal monochromator in the diffracted beam. Balanced filters present still another option.

Monochromating Crystal

With a diffractometer one has the option, which does not exist with a powder camera, of placing a crystal monochromator in the diffracted, rather than the incident, beam. Figure 7-28 shows such an arrangement. The diffracted beam from the specimen comes to a focus at the receiving slit S_1 , diverges to the focusing monochromator M , and comes to a focus again at the counter slit S_2 . Counter, crystal, and slits are mounted on one support and rotate as a unit about the diffractometer axis.

Even though intensity is decreased during diffraction by a monochromator, a $K\beta$ filter is not needed because the monochromator is set to diffract only $K\alpha$ radiation. As a result, and because of the focusing action of the monochromator, the intensity of a diffraction line at the counter can actually be higher with a monochromator than without, particularly if the monochromating crystal is graphite.

Placement of the monochromator in the diffracted beam has the advantage of suppressing background radiation originating in the *specimen*, such as fluorescent radiation and incoherent (Compton modified) scattered radiation. For example, if a steel specimen or any iron-rich material is examined with copper radiation in an ordinary diffractometer, the background due to fluorescent Fe K radiation will be unacceptably high. But if a monochromator is added and oriented to reflect only Cu $K\alpha$, the background is reduced practically to zero, because the fluoresced Fe $K\alpha$ and Fe $K\beta$ do not enter the counter. A monochromator may therefore

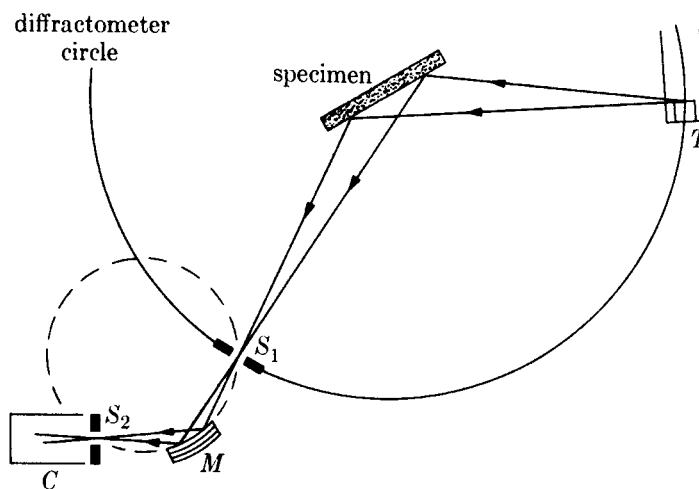


Fig. 7-28 Diffractometer with monochromating crystal M in diffracted beam. C = counter, T = x-ray tube.

eliminate the need for an extra tube, such as a Cr-target tube, for the examination of steel specimens.

The diffractometer in Fig. 15-10(a) is equipped with a diffracted-beam monochromator.

Balanced Filters

Another method of operating under essentially monochromatic conditions, a method peculiar to the diffractometer, is by the use of *Ross filters*, also called balanced filters [G.39, Vol. 3 of G.11]. This method depends on the fact that the absorption coefficients of all substances vary in the same way with wavelength; i.e., they are proportional to λ^3 , as shown by Eq. (1-13). If filters are made of two substances differing in atomic number by one, and their thicknesses adjusted so that they produce the same absorption for a particular wavelength, then they will have the same absorption for all wavelengths *except* those lying in the narrow wavelength region between the K absorption edges of the two substances. This region is called the *pass band* of the filter combination. If these filters are placed alternately in a heterochromatic x-ray beam, i.e., a beam containing rays of different wavelengths, then the difference between the intensities transmitted in each case is due only to wavelengths lying in the pass band. When the pass band is chosen to include a strong characteristic component of the spectrum, then the net effect is that of a strong monochromatic beam.

The isolation of Cu $K\alpha$ radiation may be taken as an example. Its wavelength is 1.542 Å, which means that cobalt and nickel can be used as filter materials since their K absorption edges (1.608 and 1.488 Å, respectively) effectively bracket the Cu $K\alpha$ line. Their linear absorption coefficients μ are plotted in Fig. 7-29(a), which shows that balancing can be obtained by making the nickel filter somewhat thinner than the cobalt one. When their thicknesses x are adjusted to the correct ratio, then $\mu_{\text{Ni}}x_{\text{Ni}} = \mu_{\text{Co}}x_{\text{Co}}$ except in the pass band, and a plot of μx versus λ has

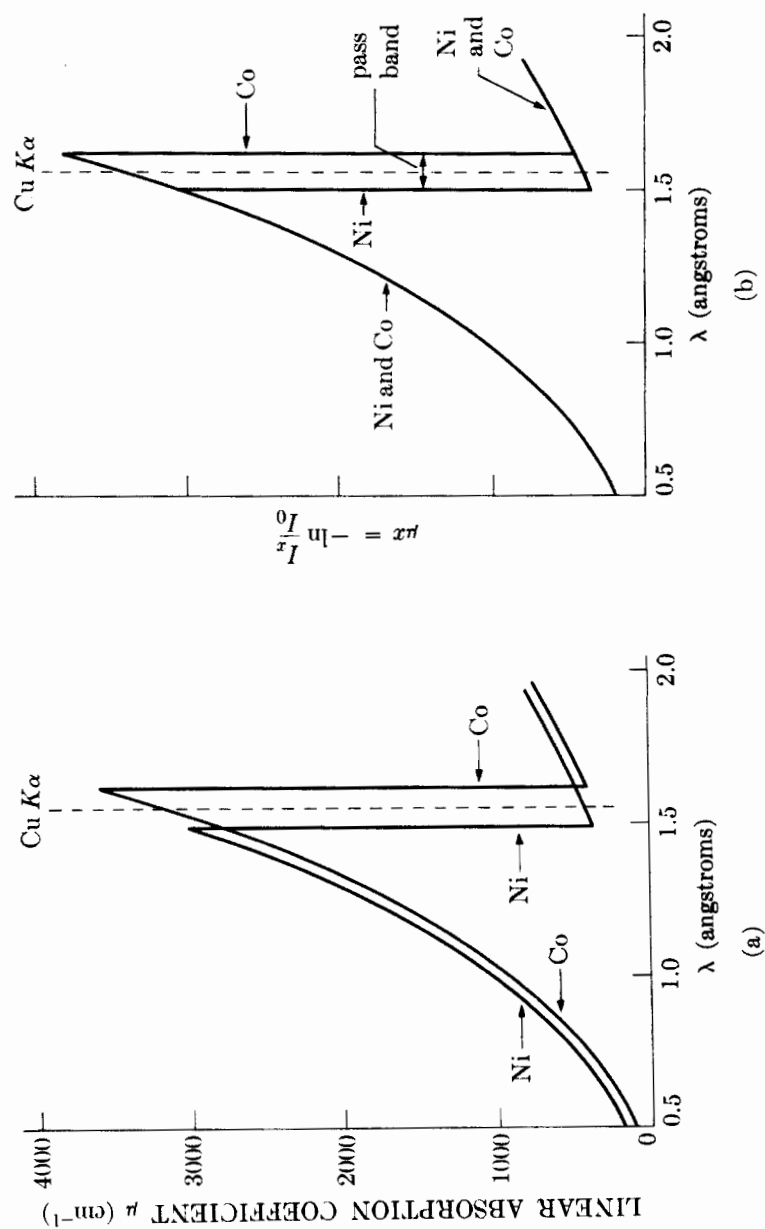


Fig. 7-29 Ross filters for Cu $K\alpha$ radiation: (a) absorption coefficients of filter materials; (b) μx values after balancing.

the appearance of Fig. 7-29(b). Since $\mu x = -\ln I_x/I_0$, the transmission factors I_x/I_0 (ratio of transmitted to incident intensity) of the two filters are now equal for all wavelengths except those in the pass band, which is only 0.12 Å wide. At each angle 2θ at which the intensity is to be measured with the diffractometer, first one filter and then the other is placed in the diffracted beam before it enters the counter. The intensity of the diffracted beam passing through each filter is then measured, and the difference in the measurements gives the diffracted intensity of only the Cu $K\alpha$ line and the relatively weak wavelengths immediately adjacent to it in the pass band.

It should be emphasized that the beam entering the counter is never physically monochromatic, as it is when a crystal monochromator is used. Radiation with a great many wavelengths enters the counter when either filter is in place, but every wavelength transmitted by one filter has the same intensity as that transmitted by the other filter, except those wavelengths lying in the pass band, and these are transmitted quite unequally by the two filters. Therefore, when the intensity measured with one filter is subtracted from that measured with the other filter, the difference is zero for every wavelength except those in the pass band.

In practice, balancing of the filters is carried out by inserting two foils of approximately the same thickness into suitable holders which can be slipped into place in the beam entering the counter. One foil is always perpendicular to the x-ray beam, while the other may be rotated about an axis at right angles to the beam; in this way the second foil may be inclined to the beam at such an angle that its effective thickness x equals the thickness required for balancing. Perfect balancing at all wavelengths outside the pass band is not possible, although it may be approached quite closely, because μ does not vary exactly as λ^3 and because the magnitude of the K absorption jump (ratio of absorption coefficients for wavelengths just shorter and just longer than the K edge) is not exactly the same for all elements.

Note also that balanced filters will not exclude Compton scattering, which differs in wavelength by only 0.05 Å or less from the wavelength of the diffracted beam (Eq. 4-3) and which will therefore generally fall inside the pass band. And if the radiation forming the diffracted beam is, for example, Cu $K\alpha$, then neither a monochromating crystal nor balanced filters will exclude diffusely scattered Cu $K\alpha$ caused, for example, by thermal vibration of the atoms.

PROBLEMS

- *7-1 A powder specimen in the form of a rectangular plate has a width of 0.5 in., measured in the plane of the diffractometer circle, which has a radius of 5.73 in. If it is required that the specimen entirely fill the incident beam at all angles and that measurements must be made to angles as low as $2\theta = 10^\circ$, what is the maximum divergence angle (measured in the plane of the diffractometer circle) that the incident beam may have?
- *7-2 Even the weather can affect the long-term stability of the measured intensity of x-rays from a well-stabilized tube, because a change in barometric pressure or humidity changes the absorption of x-rays by air. What is the percent change in the measured

intensity of Cr $K\alpha$ resulting from a 3-percent drop in pressure over a 12-hour period, a not uncommon event? (Assume a path length in air of 27 cm and take μ of air for Cr $K\alpha = 3.48 \times 10^{-2} \text{ cm}^{-1}$.)

7-3 Cu $K\alpha$ radiation is incident on a xenon-filled proportional counter. Calculate the ratio of the average pulse size in the escape peak to that in the normal peak. Compare your result with that of Fig. 7-22(b).

*7-4 If a count N_P of 30,000 is obtained at the peak of a diffraction line and, in the same time, a count N_B of 10,000 in the background adjacent to the line, calculate the percent probable error in (a) N_P and (b) $(N_P - N_B)$.

7-5 A diffraction pattern of polycrystalline platinum is obtained by energy-dispersive diffractometry at $\theta = 10.7^\circ$. Calculate the energy (in keV) at which the 2 2 0 line will appear and compare your result with Fig. 7-23(b).

*7-6 (a) Calculate the ratio of the effective thicknesses of cobalt and nickel filters when they are balanced for all wavelengths except Cu $K\alpha$. (Obtain an average value applicable to a wavelength range extending from about 0.5 Å to about 2 Å.)

b) When the filters are balanced, calculate the ratio of the intensity of Cu $K\alpha$ radiation transmitted by the nickel filter to that transmitted by the cobalt filter, assuming the same incident intensity in each case. The effective thickness of the nickel filter is 0.00035 in.