Chemical Analysis by X-ray Spectrometry

15-1 INTRODUCTION

We saw in Chap. 1 that any element, if made the target in an x-ray tube and bombarded with electrons of high enough energy, would emit a characteristic line spectrum. The most intense lines of this spectrum are the $K\alpha$ and $K\beta$ lines. They are always called “characteristic lines” to emphasize the fact that their wavelengths are fixed and characteristic of the emitting element. We also saw that these same lines would be emitted if the element were bombarded with x-rays of high enough energy (fluorescence).

In these phenomena we have the basis for a method of chemical analysis. If the various elements in the sample to be analyzed are made to emit their characteristic lines by electron or x-ray bombardment, then these elements may be identified by analyzing the emitted radiation and showing that these specific wavelengths are present. The analysis is carried out in an x-ray spectrometer of either of the following kinds:

1. **Wavelength-dispersive.** The radiation emitted by the sample is diffracted by lattice planes of known $d$ spacing in a single crystal. In accordance with the Bragg law, radiation of only a single wavelength is reflected for each angular setting of the crystal, and the intensity of this radiation can be measured with a suitable counter, as in Fig. 15-1(a). Because radiation of various wavelengths is physically dispersed in different directions in space, this method is sometimes simply called dispersive. A wavelength-dispersive spectrometer is also called a crystal spectrometer.

2. **Energy-dispersive.** In this spectrometer, diffraction is not involved. The various wavelengths in the radiation emitted by the sample are separated on the basis of their energies by means of a Si(Li) counter and a multichannel analyzer (MCA); this counter produces pulses proportional in height to the energies in the incident beam, and the MCA then sorts out the various pulse heights, as in Fig. 15-1(b). Because there is no physical separation in space of the various wavelengths (energies), such a spectrometer is often simply called nondispersive. It is more recent and less common than the crystal spectrometer.

Two kinds of x-ray spectrometry are possible, depending on the means used to excite the characteristic radiation of the elements in the sample:

1. **X-ray excitation.** The sample is bombarded with x-rays from an x-ray tube
Fig. 15-1 X-ray fluorescence spectrometers. In this example, elements 1 and 2 in the sample emit characteristic wavelengths $\lambda_1$ and $\lambda_2$. These wavelengths are separately measured by crystal diffraction in (a) or by pulse-height analysis in (b), where MCA = multichannel analyzer.

(Fig. 15-1). The primary radiation causes the sample to emit secondary fluorescent radiation, which is then analyzed in a spectrometer. This method, often called fluorescence analysis, is very widely used in industry for chemical analysis. The phenomenon of fluorescence, which is just a nuisance in diffraction experiments, is here made to serve a useful purpose.

2. Electron excitation. The sample is bombarded with high-speed electrons in an evacuated apparatus. Historically, this was the first method and was used by Moseley in his work on the relation between characteristic wavelength and atomic number. It is not a practical method for the rapid analysis of many samples, because the apparatus must be evacuated after the insertion of each sample. However, x-ray spectrometers with electron excitation are used in certain instruments of a research nature: in the electron probe microanalyzer (Sec. 15-11) and, as an optional accessory, in the transmission electron microscope and the scanning
electron microscope. These devices, incidentally, are often called electron-column instruments.

Chemical analysis by x-ray spectrometry can be either qualitative, if the various characteristic lines in the emitted spectrum are simply identified, or quantitative, if the intensities of these lines are compared with the intensities of lines from a suitable standard. Note that x-ray spectrometry gives information about the chemical elements present in the sample, irrespective of their state of chemical combination or the phases in which they exist. X-ray diffraction, on the other hand, as we saw in the previous chapter, discloses the various compounds and phases present in the sample. Spectrometry and diffraction therefore complement one another in the kind of information they provide.

X-ray spectrometry by fluorescence analysis is nondestructive and much more rapid than the ordinary wet methods of chemical analysis. Automatic instruments exist and are widely used in industry for the analysis of such disparate materials as alloys, ores, cements, and petroleum products.

X-ray spectrometry is of such wide interest today as a means of chemical analysis that it has been given book-length treatment by several authors: Jenkins and DeVries [G.29], Birks [G.31], Jenkins [G.41], and Bertin [G.46]. In addition, a book by Jenkins [G.37] presents worked-out problems arising in practical spectrometry, and [7.18] contains many papers on energy-dispersive methods and microanalysis.

15-2 GENERAL PRINCIPLES

Except for Sec. 15-11, this chapter is devoted entirely to fluorescence analysis, i.e., to x-ray excitation of the elements in the sample. We must therefore examine the excitation process itself in some detail.

The fluorescent radiation emitted by the sample should be as intense as possible, so that it will be accurately measurable in a short counting time. The intensity of this emitted radiation depends on both the wavelength and the intensity of the incident primary radiation from the x-ray tube. Suppose that monochromatic radiation of constant intensity and of wavelength \( \lambda \) is incident on an element which has a K absorption edge at \( \lambda_K \), and that we can continuously vary \( \lambda \). As we decrease \( \lambda \) from a value larger than \( \lambda_K \), no K fluorescence occurs until \( \lambda \) is just shorter than \( \lambda_K \). The fluorescent intensity is then a maximum. Further decrease in \( \lambda \) causes the fluorescent intensity to decrease, in much the same manner as the absorption coefficient. This is natural since, as mentioned in Sec. 1-5, fluorescence and true absorption are but two aspects of the same phenomenon. At any one value of \( \lambda \), the fluorescent intensity is directly proportional to the incident intensity.

The best exciting agent would therefore be a strong characteristic line of wavelength just shorter than \( \lambda_K \). It is clearly impossible to satisfy this requirement for more than one fluorescing element at a time, and in practice we use a tube with a tungsten, or other heavy metal, target or a chromium target, with as high a power rating as possible. The exciting radiation is then that part of the continuous spectrum and such characteristic lines of the target as have shorter wavelengths.
than the absorption edge of the fluorescing element. Tube choice depends on the elements to be most often determined: a W tube will give higher fluorescent intensities from heavy elements and a Cr tube from light elements. One manufacturer supplies a dual-target tube, from which either W or Cr radiation can be obtained at the turn of a switch without breaking the tube vacuum.

The fluorescent yields $\omega$ of the elements in the sample are also relevant here. As we saw in Sec. 1-5, fluorescent radiation and the ejection of an Auger electron are competing processes, and the Auger effect is more important for light elements. For elements lighter than Cl (atomic number $Z = 17$) the probability of $K$ fluorescence is less than 10 percent.

The beam of secondary radiation issuing from the sample consists largely of fluorescent radiation, but there are some other weak components present as well. These are coherent scattered radiation, coherent diffracted radiation, and incoherent (Compton modified) radiation. These components appear as a background on which the spectral lines are superimposed. This background is normally low (see Fig. 15-3), but it may become rather high if the sample contains a large proportion of elements of low atomic number, because the sample will then emit a large amount of Compton modified radiation.

The wavelength range used in fluorescence analysis extends from about 0.2 Å to 20 Å. The lower limit is imposed mainly by the maximum voltage that can be applied to the x-ray tube, which lies in the range 50–100 kV in commercial instruments. At 100 kV the short-wavelength limit of the continuous spectrum from the tube is $12.4/100 = 0.12$ Å. The maximum intensity occurs at about 1.5 times this value, or 0.18 Å. Incident radiation of this wavelength would cause $K$ fluorescence in Hf ($Z = 72$), and the emitted $K\alpha$ radiation would have a wavelength of 0.22 Å. For heavier elements we can use $L$ rather than $K$ lines; thus the lower limit on $\lambda$ does not impose any upper limit on the atomic number $Z$ of detectible elements. Figure 15-2 shows how the wavelength of the strongest $K$ and $L$ lines varies with atomic number.

The upper limit on wavelength depends on the equipment available and is imposed by the large absorption of long-wavelength fluorescent radiation by anything it encounters, such as air and the counter window. Absorption therefore puts an unfortunate lower limit on the detectible light elements. If the spectrometer operates in air, Ti ($Z = 22$, $K\alpha = 2.75$ Å) is about the lightest element detectible. ($Ti\ K\alpha$ radiation is decreased to one half its original intensity by passage through only 10 cm of air.) If a path filled with helium is provided for the x-rays traversing the spectrometer, absorption is decreased to such an extent that Al is measurable ($Z = 13$, $K\alpha = 8.3$ Å). In commercial vacuum spectrometers the usual lower limit is F ($Z = 9$, $K\alpha = 18.3$ Å). (The vacuum requirement in the sample chamber of a fluorescent spectrometer is not nearly as severe as in an electron-excitation instrument. Therefore, the pump-down time after sample insertion is much shorter in the former.)

Another important factor which limits the detection of light elements is absorption in the sample itself. Fluorescent radiation is produced not only at the surface of the sample but also in its interior, to a depth depending on the depth of
Fig. 15–2  Variation with atomic number \( Z \) of the wavelength and energy of the strongest emission lines of the \( K \) and \( L \) series.

effective penetration by the primary beam, which in turn depends on the overall absorption coefficient of the sample. The fluorescent radiation produced within the sample then undergoes absorption on its way out. Because long-wavelength fluorescent radiation will be highly absorbed by the sample, the fluorescent radiation outside the sample comes only from a thin surface skin and its intensity is accordingly low. It follows that detection of small amounts of a light element in a heavy-element matrix is practically impossible. On the other hand, even a few parts per million of a heavy element in a light-element matrix can be detected.

**WAVELENGTH DISPERSION**

**15–3 SPECTROMETERS**

In one type of spectrometer, called single-channel, the analyzing crystal and counter are mechanically coupled, as in a diffractometer. Thus, when the crystal is set at a particular Bragg angle \( \theta \), the counter is automatically set at the corresponding angle \( 2\theta \). With the counter connected to a ratemeter and recorder, the whole spectrum can be continuously scanned and recorded.

Figure 15–3(a) shows an example of such a scan. It looks a lot like a powder pattern made with a diffractometer, for example, Fig. 7–5. However, the lines of a powder pattern are reflections of the same wavelength from planes of different indices \( hkl \), whereas the lines in Fig. 15–3(a) all have the same indices (those of the (200) reflecting planes of the analyzing crystal) but each is formed by a different wavelength. That wavelength is calculable from the Bragg angle and the interplanar spacing of the crystal.
Chemical analysis by x-ray spectrometry

Fig. 15-3 Recording of fluorescent spectrum of a stainless steel containing 19.4 Cr, 9.5 Ni, 1.5 Mo, 1.4 W, 1.0 Mn (in weight percent), balance mainly Fe. Flat LiF crystal analyzers. Platinum-target x-ray tube, 50 kV, 40 mA. (Courtesy of Diano Corporation.)

The spectrum in Fig. 15–3(a) is that of a stainless steel, excited by the primary beam from a platinum-target x-ray tube. The K lines of all the major constituents (Fe, Cr, and Ni) and of some of the minor constituents (Mo and Mn) are apparent. One of the L lines of W is also present. The Cu Kα line originates from copper existing as an impurity in the tube target. Figure 15–3(b), a recording made at higher resolution, is discussed later.

X-ray Optics

The analyzing crystal may be flat or curved, with resulting differences in spectrometer design.

The flat-crystal type, illustrated in Fig. 15–4, has the simpler design. The x-ray tube is placed as close as possible to the sample, so that the primary radiation on it, and the fluorescent radiation it emits, will be as intense as possible. For the operator’s protection against scattered radiation, the sample is enclosed in a thick metal box, which contains a single opening through which the fluorescent beam leaves. The sample area irradiated is of the order of 2 cm square. Fluorescent
radiation is emitted in all directions by this area, which acts as a source of radiation for the spectrometer proper. Because of the large size of this source, the beam of fluorescent radiation issuing from the protective box contains a large proportion of widely divergent and convergent radiation. Collimation of this beam before it strikes the analyzing crystal is therefore absolutely necessary, if any resolution at all is to be obtained. This collimation is achieved by passing the beam through a Soller slit whose plates are at right angles to the plane of the spectrometer circle, because it is the divergence (and convergence) in this plane that we want to eliminate.

Essentially parallel radiation from the collimator is then incident on the flat crystal, and a portion of it is diffracted into the counter by lattice planes parallel to the crystal face. Because no focusing occurs, the beam diffracted by the crystal is fairly wide and the counter receiving slit must also be wide.

The *curved-crystal* spectrometer is illustrated in Fig. 15-5. Radiation from the sample passes through the narrow slit \( S \) and diverges to the analyzing crystal, which has its reflecting planes bent to a radius of \( 2R \) and its surface ground to a radius \( R \). Diffracted radiation of a single wavelength is brought to a focus at the counter receiving slit, located on the focusing circle passing through \( S \) and the face of the crystal, as described in Sec. 6-13. But now the radius \( R \) of the focusing circle is fixed, for a crystal of given curvature, and the slit-to-crystal and crystal-to-focus distances must both be varied as \( \theta \) is varied. The focusing relation, found from Eq. (6-13), is

\[
D = 2R \sin \theta,
\]

where \( D \) stands for both the slit-to-crystal and crystal-to-focus distances, which must be kept equal to one another. This is accomplished by rotation of both the crystal and the counter about the center \( O \) of the focusing circle, in such a manner that rotation of the crystal through an angle \( \chi \) (about \( O \)) is accompanied by rotation of the counter through an angle \( 2\chi \). At the same time the counter is rotated about
Fig. 15-5 X-ray spectrometer, curved-crystal type.

a vertical axis through its slit, by means of another coupling, so that it always points at the crystal.

$D$ increases as $\theta$ increases and may become inconveniently large, for a crystal of given radius of curvature $R_1$, at large $\theta$ values. In order to keep $D$ within reasonable limits, it is necessary to change to another crystal, of smaller radius $R_2$, for this high-$\theta$ (long-wavelength) range.

Crystals

The angle $2\theta$ at which a particular wavelength is reflected depends only on the $d$ spacing of the analyzing crystal. The Bragg law shows that the longest wavelength that can be reflected is equal to $2d$. We therefore need crystals with small $d$ spacings for short wavelengths (high-Z elements) and large $d$ spacings for long wavelengths (low-Z elements). Table 15-1, after Jenkins [G.41], lists the most commonly used crystals, and Bertin [G.46] gives a much longer list.

Other factors affecting the choice of a crystal are its reflecting power and resolving power. These properties are discussed later.

Counters

The scintillation counter (Sec. 7-7) and the sealed gas proportional counter (Sec. 7-5) are both used in spectrometry. The scintillation counter is better for the very short wavelength region because of its greater efficiency there (Fig. 7-12); in the 1 Å–2 Å range either counter is suitable. In the long-wavelength region a gas-flow proportional counter is required, because of its thin low-absorption window.
### Table 15-1

Analyzing Crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Reflecting plane</th>
<th>2(d(\theta))</th>
<th>Usual atomic number range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium fluoride (LiF)</td>
<td>(420)</td>
<td>1.80</td>
<td>high Z, high resolution</td>
</tr>
<tr>
<td>Lithium fluoride (LiF)</td>
<td>(200)</td>
<td>4.03</td>
<td>all Z &gt; 19</td>
</tr>
<tr>
<td>Germanium (Ge)</td>
<td>(111)</td>
<td>6.53</td>
<td>(no 222 reflection)*</td>
</tr>
<tr>
<td>Pyrolytic graphite (PG)</td>
<td>(002)</td>
<td>6.72</td>
<td>P(15), S(16), and Cl(17)</td>
</tr>
<tr>
<td>Pentacrylthirol (PET)</td>
<td>(002)</td>
<td>8.74</td>
<td>Al(13) through K(19)</td>
</tr>
<tr>
<td>Ammonium dihydrogen phosphate (ADP)</td>
<td>(101)</td>
<td>10.64</td>
<td>Mg(12)</td>
</tr>
<tr>
<td>Rubidium acid phthalate (RAP)</td>
<td>(001)</td>
<td>26.1</td>
<td>F(9) and Na(11)</td>
</tr>
</tbody>
</table>

* Ge has no 222 (second-order 111) reflection (Sec. 6-13). Second-order reflections sometimes cause line-overlap problems. See text.

Some counters have two windows in line. The beam from the crystal passes through a gas-flow counter, with two side windows opposite one another, and then strikes a scintillation counter. By collecting pulses from both counters, high sensitivity to both long and short wavelengths is achieved.

A single-channel pulse-height analyzer (Sec. 7-9) in the counting circuit may be useful in dealing with interfering high-order reflections (harmonics) \[^{[G.29]}\]. If the crystal is set to diffract spectral line \(\lambda_A\) from element A in the sample, it will also diffract, at the same angle \(\theta\), wavelengths \(\lambda_A/2\) in the second order, \(\lambda_A/3\) in the third order, etc. If the sample also emits line \(\lambda_B\) from element B, and if \(\lambda_B\) happens to equal \(\lambda_A/2\), then the condition called harmonic overlap exists and the counter is receiving two spectral lines simultaneously. As a specific example, suppose a sample contains phosphorus (P \(K\alpha = 6.16\) Å) and calcium (Ca \(K\beta = 3.09\) Å). When the crystal is set to diffract P \(K\alpha\), it will also diffract Ca \(K\beta\) in the second order at very nearly the same angle. But the counter pulses from these two wavelengths will be of different sizes, and the window of the pulse-height analyzer can be set to pass the P \(K\alpha\) pulses and exclude the Ca \(K\beta\) pulses. (An alternate solution would be to use a germanium crystal as analyzer; as mentioned in Table 15-1, its (111) planes do not produce a second-order reflection.)

The escape-pulse phenomenon described in Sec. 7-9 is also relevant here and should be kept in mind when using a pulse-height analyzer.

### Single-Channel Spectrometers

The spectrometers shown in Figs. 15-1(a), 15-4, and 15-5 are single-channel instruments, in the sense that they have only one counter, which is regarded as a “channel” through which information is received. The various spectral lines are measured sequentially by moving the counter from one line to another, either manually or by a mechanical drive.

In automatic single-channel spectrometers, the angular positions \(2\theta_A, 2\theta_B, \ldots\), at which lines \(\lambda_A, \lambda_B, \ldots\) will be reflected, are preset; the counter moves rapidly to position \(2\theta_A\), remains there long enough to make an accurate intensity measurement, swings rapidly to \(2\theta_B\), etc. After each measurement the total counts received
are recorded on a print-out device or sent to a computer (Sec. 15-6) for conversion to percent concentration of the element involved. A large number of line positions $2\theta$ can be programmed, and automatic sample changers can sequentially put up to 60 samples into position. Unattended analysis of many samples for many elements is therefore possible.

**Multichannel Spectrometers**

These are automatic instruments which have as many channels (crystals and counters) as there are spectral lines to be measured. In each channel a crystal and counter are fixed at the correct angular positions to measure a selected spectral line, such as line $\lambda_A$ from element A. A number of channels are arranged in a circle around a centrally located x-ray tube (Fig. 15-6). All the analyzing channels receive the same fluorescent radiation from the sample, while one nondispersive control channel receives fluorescent radiation directly from a standard. The control channel serves to monitor the output of the x-ray tube. Some instruments have as many as 30 channels.

When a sample is being analyzed, all counters are started simultaneously. When the control channel has accumulated a predetermined number of counts, all counters are automatically stopped and the number of counts collected by each counter is recorded. Because the total fluorescent energy received in each analyzing counter is related to a fixed amount of energy entering the control counter, variations in the x-ray tube output do not affect the accuracy of the results.

The kind of crystal and kind of counter in each channel are selected to be best suited to the wavelength to be measured in that channel. No compromise has to be made in order to cover a certain wavelength range, as in a single-channel instrument.

Because all channels operate simultaneously, a multichannel instrument is fast.

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**Fig. 15-6** Multichannel spectrometer, curved-crystal type, with relative arrangement of x-ray tube, sample, and one analyzing channel. (The tube shown is of the end-window type: the face of the target is inclined to the tube axis and the x-rays produced escape through a window in the end of the tube. Other spectrometers of this kind use a side-window x-ray tube.)
Fig. 15-7 Multichannel crystal spectrometer. (a) Overall view. (b) Close-up view of end-window x-ray tube and several analyzing channels; the crystal and counter of one channel are indicated; this entire enclosure is evacuated. (Courtesy of Applied Research Laboratories.)
A complete analysis for many elements, including print-out of the results, takes about one minute.

Multichannel spectrometers may contain, in addition to the fixed channels, a scanning channel in which a moving crystal and counter can sequentially scan the entire spectrum, just as in a single-channel instrument. This feature is useful for qualitative analysis or for quantitative determination of an element for which a fixed channel has not been preset.

Multichannel spectrometers are made by several manufacturers. Figure 15–7 shows one example.

### 15-4 INTENSITY AND RESOLUTION

In any spectrometer the attainment of adequate intensity and adequate resolution are important problems. The intensity of the fluorescent radiation emitted by the sample is very much less than that of the primary radiation incident on it, and can become very low indeed when the fluorescing element is only a minor constituent of the sample. This fluorescent radiation is then diffracted by the analyzing crystal, and another large loss of intensity occurs, because diffraction is such an inefficient process. The diffracted beam entering the counter may therefore be very weak, and a long counting time will be necessary to measure its intensity with acceptable accuracy. Spectrometer design must therefore ensure maximum intensity of the radiation entering the counter. At the same time, the spectrometer must be capable of high resolution, if the sample contains elements which have characteristic lines of very nearly the same wavelength and which must be separately identified. Both these factors, intensity and resolution, are affected by the kind of analyzing crystal used and by other details of spectrometer design.

Curved analyzing crystals, because of their focusing action, give greater intensity than flat crystals.

As we saw in Fig. 6–10, resolution depends both on $\Delta 2\theta$, the dispersion, or separation, of line centers, and on $B$, the line breadth at half-maximum intensity. The resolution will be adequate if $\Delta 2\theta$ is equal to or greater than $2B$. By differentiating the Bragg law, we obtain

$$\frac{\lambda}{\Delta \lambda} = \frac{2 \tan \theta}{\Delta 2\theta}.$$  \hspace{1cm} (15-1)

When the minimum value of $\Delta 2\theta$, namely $2B$, is inserted, this becomes

$$\frac{\lambda}{\Delta \lambda} = \frac{\tan \theta}{B}.$$  \hspace{1cm} (15-2)

The left-hand side of this equation gives the resolving power required to separate two lines of mean wavelength $\lambda$ and wavelength difference $\Delta \lambda$. The right-hand side gives the resolving power available, and this involves both the mean Bragg angle of the lines and their breadth. Note that the available resolving power increases rapidly with $\theta$, for a given line breadth. This means that, of two crystals producing the same line breadth, the one with the smaller plane spacing $d$ will have the greater