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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).

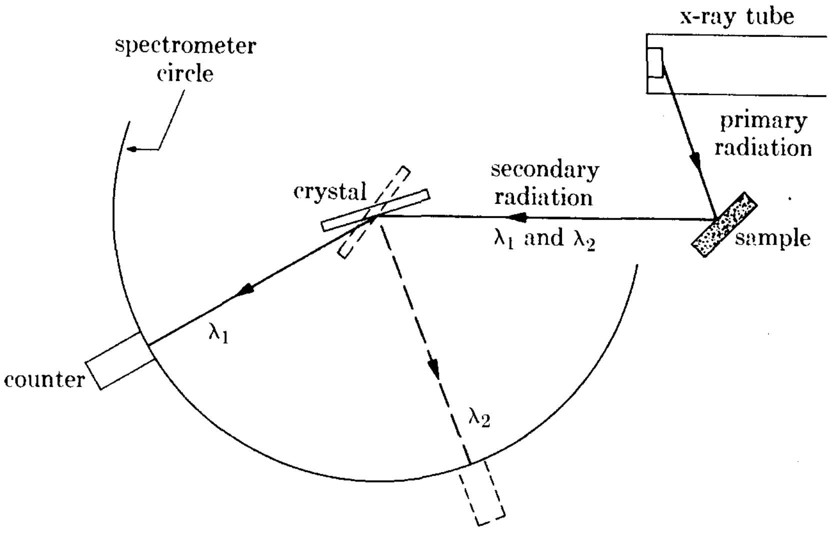
In these phenomena we have the basis for a method of chemical analysis. If the various elements in the sample to be analyzed are made to emit their characteristic lines by electron or x-ray bombardment, then these elements may be identified by analyzing the emitted radiation and showing that these specific 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.*

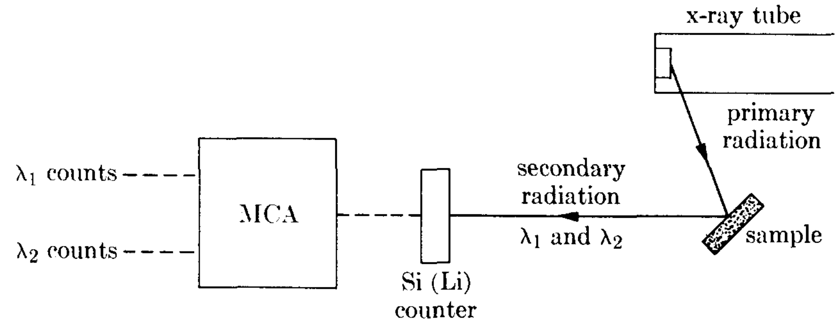
2. *Energy-dispersive.* In this spectrometer, diffraction is not involved. The various wavelengths in the radiation emitted by the sample are separated on the basis of their energies by means of a Si(Li) counter and a multichannel analyzer (MCA); this counter produces pulses proportional in height to 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



(a) Wavelength-dispersive spectrometer



(b) Energy-dispersive spectrometer

Fig. 15-1 X-ray fluorescence spectrometers. In this example, elements 1 and 2 in the sample emit characteristic wavelengths λ_1 and λ_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 λ is incident on an element which has a K absorption edge at λ_K, and that we can continuously vary λ. As we decrease λ from a value larger than λ_K, no K fluorescence occurs until λ is just shorter than λ_K. The fluorescent intensity is then a maximum. Further decrease in λ 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 λ, 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 λ_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 ω 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 λ 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 commerical 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

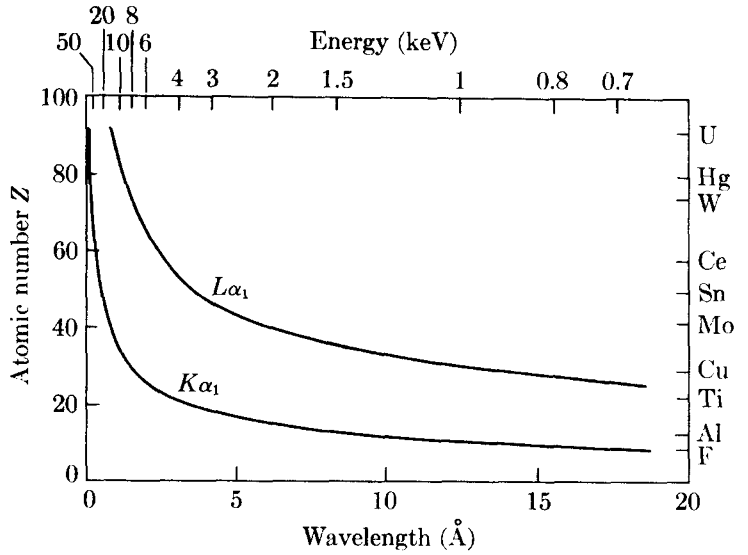


Fig. 15-2 Variation with atomic number Z of the wavelength and energy of the strongest emission lines of the K and L series.

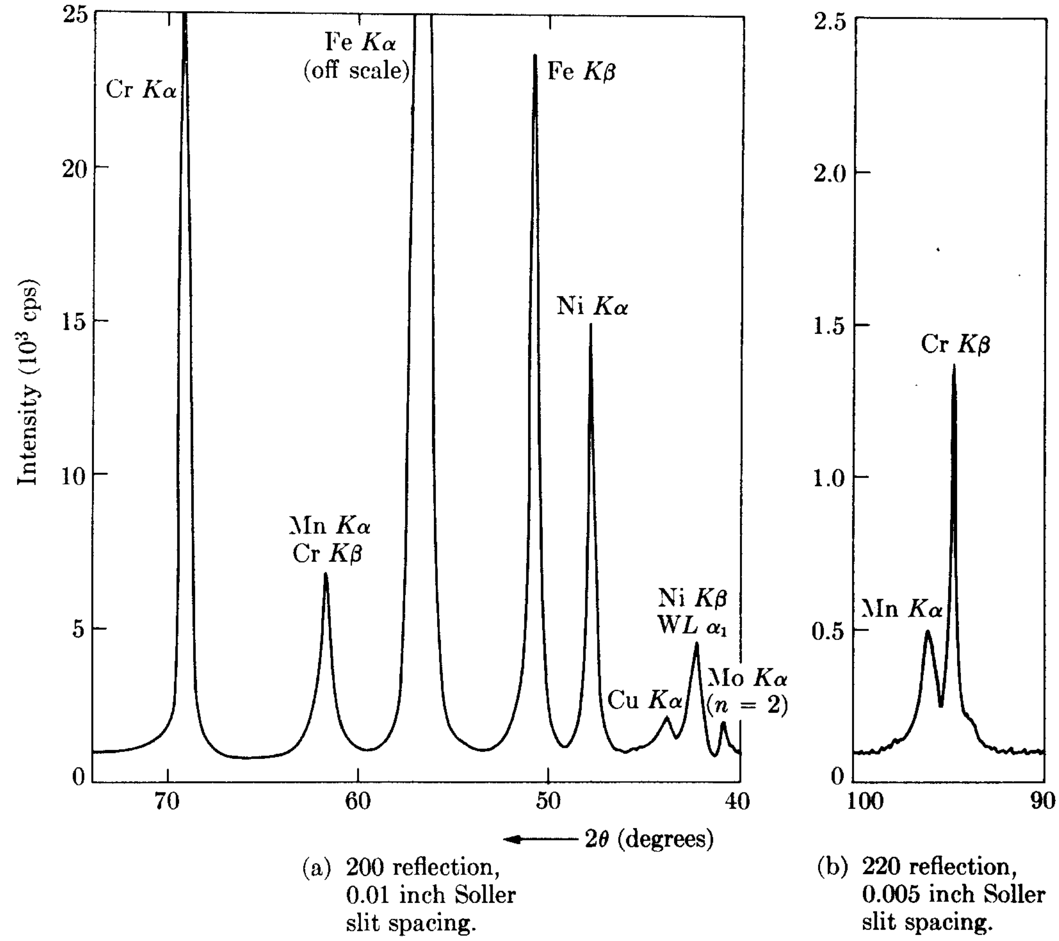
effective penetration by the primary beam, which in turn depends on the overall absorption coefficient of the sample. The fluorescent radiation produced within the sample then undergoes absorption on its way out. Because long-wavelength fluorescent radiation will be highly absorbed by the sample, the 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 θ, the counter is automatically set at the corresponding angle 2θ. 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.



(a) 200 reflection, 0.01 inch Soller slit spacing.

(b) 220 reflection, 0.005 inch Soller slit spacing.

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

$2d = 2.85$ Å, $B = 0.5°$) separates the lines enough for identification. If, in addition, the collimation is improved to an estimated B of 0.4°, the resolving power becomes 155, and the lines are well separated [Fig. 15-3(b)]. [An equivalent way of estimating resolution is to calculate the dispersion $\Delta 2\theta$ produced by a given crystal and compare it with the dispersion required, namely, $2B$. The value of $\Delta 2\theta$ is given by $(2 \tan \theta)(\Delta\lambda/\lambda)$, from Eq. (15-1).]

To sum up, high intensity is desirable in fluorescent analysis in order that the counting time required to obtain good accuracy be reasonably short; if the element to be detected is present only in small concentrations and a crystal of low reflecting power is used, the required counting times will be prohibitively long. High resolution is desirable whenever the analysis requires use of a spectral line having very nearly the same wavelength as another line from the sample or the x-ray tube target.

15-5 QUALITATIVE ANALYSIS

In qualitative work sufficient accuracy can be obtained by automatic scanning of the spectrum, with the ratemeter output fed to a chart recorder. Interpretation of the recorded spectrum will be facilitated if the analyst has on hand (a) a table of corresponding values of λ and 2θ for the particular analyzing crystal used, and (b) a single table of the principal K and L lines of all the elements arranged in numerical order of wavelength. Such a wavelength table is given in Vol. 4 of [G.11] and is much more useful than one, like that in Appendix 7, in which K and L lines are listed separately in order of atomic number.

Since it is important to know whether an observed line is due to an element in the sample or to an element in the x-ray tube target, a preliminary investigation should be made of the spectrum emitted by the target alone. For this purpose a substance like carbon or a plastic is placed in the sample holder and irradiated in the usual way; such a substance merely scatters part of the primary radiation into the spectrometer, and does not contribute any observable fluorescent radiation of its own. The spectrum so obtained will disclose the characteristic lines of the target and of any impurities it may contain.

15-6 QUANTITATIVE ANALYSIS

In the absence of interfering effects one would expect that the intensity I_A of a fluorescent line from element A in the sample would be directly proportional to the atomic fraction of A present. But interfering effects do exist; they are not trivial; and the fluorescent intensity can depart widely from proportionality to the amount present. Examples are shown in Fig. 15-8 for three binary mixtures containing iron. These curves demonstrate that the fluorescent intensity from a given element depends markedly on the other element or elements present.

This behavior is due chiefly to two effects:

1. *Matrix absorption.* As the composition of the sample changes, so does its absorption coefficient. As a result there are changes both in the absorption of the

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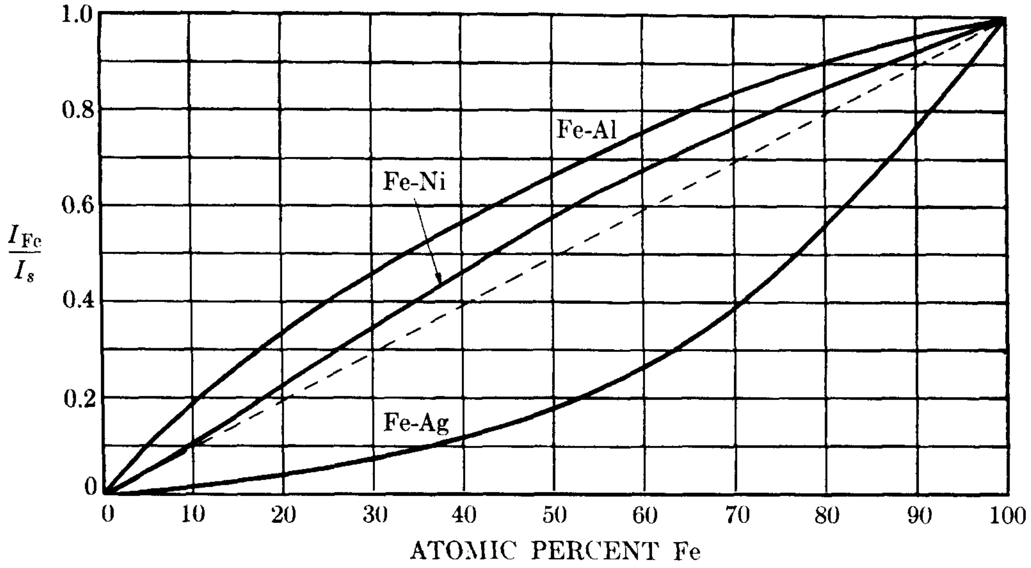

Fig. 15-8 Effect of iron concentration on the intensity of Fe $K\alpha$ radiation fluoresced by various mixtures. I_{Fe} and I_s are the Fe $K\alpha$ intensities from the mixture and from pure iron, respectively. Friedman and Birks [15.1].

primary radiation traveling into the sample and in the absorption of the fluorescent radiation traveling out. The absorption of the primary radiation is difficult to calculate, because the part of that radiation effective in causing K fluorescence, for example, in A has wavelengths extending from λ_{SWL}, the short-wavelength limit of the continuous spectrum, to λ_{KA}, the K absorption edge of A. To each of these incident wavelengths corresponds a different incident intensity and a different matrix absorption coefficient. The absorption of the fluorescent radiation, of wavelength λ_A, depends only on the absorption coefficient of the specimen for that particular wavelength. (Absorption effects are particularly noticeable in the Fe-Al and Fe-Ag curves of Fig. 15-8. The absorption coefficient of an Fe-Al alloy is less than that of an Fe-Ag alloy of the same iron content, with the result that the depth of effective penetration of the incident beam is greater for the Fe-Al alloy. A larger number of iron atoms can therefore contribute to the fluorescent beam, and this beam itself will undergo less absorption than in the Fe-Ag alloy. The over-all result is that the intensity of the fluorescent Fe $K\alpha$ radiation outside the specimen is greater for the Fe-Al alloy.)

2. *Enhancement* (*multiple excitation*). If the primary radiation causes element B in the specimen to emit its characteristic radiation, of wavelength λ_B, and if λ_B is less than λ_{KA}, then fluorescent K radiation from A will be excited not only by the incident beam but also by fluorescent radiation from B. (This effect is evident in the Fe-Ni curve of Fig. 15-8. Ni $K\alpha$ radiation can excite Fe $K\alpha$ radiation, and the result is that the observed intensity of the Fe $K\alpha$ radiation from an Fe-Ni alloy is closer to that for an Fe-Al alloy of the same iron content than one would expect from a simple comparison of the absorption coefficients of the two alloys. In the case of an Fe-Ag alloy, the observed Fe $K\alpha$ intensity is much lower, even though Ag $K\alpha$ can excite Fe $K\alpha$, because of the very large absorption in the specimen.)

These effects so complicate the calculation of fluorescent intensities that quantitative analysis is usually performed on an empirical basis, i.e., by the use of standard samples of known composition. These samples need not cover the 0–100 percent range, as in Fig. 15–8, but only quite limited ranges, because the greatest use of fluorescent analysis is in control work, where a great many samples of approximately the same composition have to be analyzed to see if their composition falls within specified limits. Standard samples of known composition, established by wet chemical analysis, may be purchased from the National Bureau of Standards [15.2] or from various commerical sources [15.3].

Three methods are used for quantitative analysis: calibration curves, empirical coefficients, and fundamental parameters.

Calibration Curves

When only a single element is to be determined and its concentration range is narrow, the matrix composition is essentially constant and so are the effects of matrix absorption and enhancement. The analytical problem is then reduced to the preparation of a single calibration curve, which is often linear. Figure 15–9 shows an example, for analysis in the parts-per-million (ppm) range. In this particular case, the background, represented by the intercept on the ordinate, is very high.

Empirical-Coefficient Method

This method, the most widely used of all, is required for such materials as alloys, cements, and ores, where typically five or more elements must be determined and where each element may vary in concentration over a substantial range. The

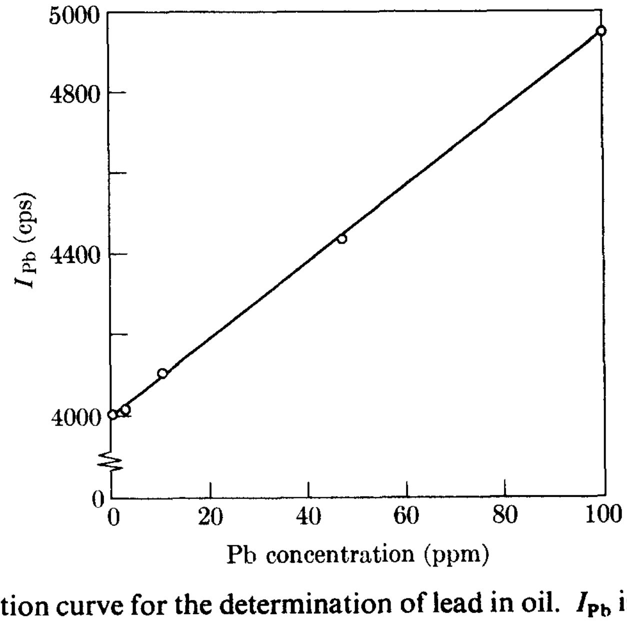

Fig. 15–9 Calibration curve for the determination of lead in oil. I_{Pb} is the intensity of the Pb $L\alpha$ line. Tungsten-target tube (40 kV, 20 mA), LiF analyzing crystal, scintillation counter. Jenkins and DeVries [G.37].