PART IV: X-RAY EMISSION SPECTROSCOPY

l. INTRODUCTION

1.1 General comments on nomenclature

Parts I and II of this series were concerned with general recommendation for atomic emission spectroscopy and the interpretation of data. They serve as a guide to Part IV on X-ray spectrochemical analysis just as they did to Part III on flame spectroscopy. The nomenclature and practices described in this document conform generally to optical spectroscopy (see Part I). There are some instances, however, where long established practice decrees the use of special symbols and terminology. For example, essentially all X-ray measurements are made by photon counting techniques but the results are seldom converted to radiant flux or irradiance or radiant exposure. The term photon flux would be appropriate if the measurements were corrected for detector efficiency but this is seldom done for X-ray chemical analysis (it is done for measurement of Bremsstrahlung spectral distributions, see Sec. 4.1). Therefore the term *X-ray intensity*, I, is commonly used and expressed as photons/unit time detected. Likewise the term *relative X-ray intensity*, I_r, is used to mean the intensity for the analyte in an unknown specimen divided by the intensity for concentration of the analyte element. As another example, the symbols used for analyzer-crystal parameters and for X-ray attenuation coefficients are well established and used consistently in the literature. They are not easily confused with symbols in other fields of spectroscopy and are therefore retained.

1.2 Similarity between X-ray and optical spectroscopy

There are some similarities but some important differences between X-ray spectroscopy and optical spectroscopy. Like any other emission spectroscopic method, X-ray spectroscopy consists of three steps: a) excitation to produce emission lines characteristic of the elements in the material, b) measurement of their intensity, and c) conversion of X-ray intensity to concentration by a calibration procedure which may include correction for matrix effects. The wavelength region of interest makes the instrumentation and requirements differ considerably, however, from other emission spectroscopic techniques.

1.3 The origin of characteristic X-ray photons

The characteristic X-ray photons used for analysis are those photons which arise from transitions between inner electron energy levels in atoms . To generate characteristic emission the atom must first be ionized in, say, the K, L, or M shell. Ionization may be accomplished by any photon or particle whose energy exceeds the binding energy of the electrons in the particular shell. After ionization, the X-ray line emission (or Auger emission, see Sec. 4.3.1) occurs when the electron vacancy is filled by an electron from one of the outer shells. The energy, E, of the characteristic photon is equal to the difference in the binding energies between the two electron levels involved in the transition. Lines are called *K series* lines if the initial ionization is in the K shell, *L series* lines if it is in the L shell and so on.

The characteristic photon may also be described by its wavelength, l where l and E are related by the expression $l = K/E$. The value of the constant, K, is 1.9865×10^{-16} nm J which is 1.2399×10^{3} nm V

2. GENERAL TERMS

The following terms are in conformance with Part I of this series of documents.

space coordinates	x, y, z
length	l
height	h
breadth (width)	b
area	S, A
volume	V
density	r
radius	r
plane angles	a, b, g
solid angle	W
speed of light (in vacuum)	$c, (c_0)$
wavelength	l
frequency	n
mass	m
time	t
energy	E
power (energy divided by time)	P
Planck's constant	h

3. TERMS RELATED TO SAMPLE

3 1 Bulk sample

Solid or liquid samples of one gram or more are generally used in X-ray spectroscopy. If the sample is thick enough so that the intensity of characteristic fluorescent radiation is not significantly modified by an increase in thickness, the sample is described as a bulk sample of *effectively infinite thickness*.

3 1.1 Solid sample

Metals or alloys have the surface flattened by grinding or abrading. Provided that the reference samples and the unknowns are prepared in the same manner, the surface roughness which can be tolerated without mathematical correction for roughness varies from about 50 µm peak-to-valley distance for atomic-number elements above Z = 25 to 10 µm for elements around Z = 12.

3.1.2 Powder sample

Minerals or ores can be prepared by packing the powder in cells with or without a binder. If powdered reference samples are employed the particle size should be similar to that of the unknowns. The particle size which can be tolerated without mathematical correction is similar to the surface roughness described in Sec. 3.1.1 for the same elements

3.1.3 Solid-solution sample

These are prepared by dissolving solids and powders in borax or similar flux to make a homogeneous sample. This procedure sacrifices intensity because of the dilution but eliminates mathematical correction for particle size or other heterogeneities in the original sample and generally reduces interelement effects.

3.1.4 Liquid sample

These are generally contained in a cell with a thin window to pass the incident and emergent X-rays. Volatile liquids may change in composition due to evaporation of one or more components.

3.2 *Sample of limited size*

If the quantity of material is too small to prepare a bulk sample the relationship between X-ray intensity and concentration for each analyte will depend on the mass of the sample as well as its composition. It is often advantageous to use only 0.5 to 1.0 mg/cm^2 or less even if a somewhat greater amount of material is avail able. For such limited quantities the X-ray intensity of the analyte is essentially linear with its concentration, independent of matrix composition.

4. TERMS RELATED TO X-RAY GENERATION

X-ray spectra characteristic of the analyte elements in a specimen may be excited by a variety of incident photons or accelerated particles. The two most frequently used types of excitation are by electrons (e.g. in electron microprobes or scanning electron microscopes) and by photons from X-ray tubes. However, other f rms of excitation also exist.

4.1 X-ray generation by electrons

When a beam of electrons strikes a target or specimen there are three ways in which the electrons may lose energy. The average energy loss per unit distance traveled along the electron path is called *electron stopping power*, dE/dx.

4.1.1 Low energy collisions

Most electron interactions with atoms result in a few eV energy loss for the electron. This loss in electron energy is transformed mainly into heat in the material irradiated.

4.1.2 Characteristic X-ray production.

A small fraction, l part in 10^3 or less of the electron interactions, ionize the atoms and may result in emission of a characteristic photon (see Section 4.3). The *cross section for ionization* by electrons, Q, describes the probability of such an ionization. Its customary unit is cm^2 and is usually given as the cross section for producing a particular kind of ionization, e.g., Q_K, Q_{LII}, etc. where the subscript refers to the shell or subshell ionized. Q is used in the equation $dA/dx = qQ_i n_i$ where q is the number of electrons per cm^2 incident normal to the thin layer of material containing n_i atoms per unit volume of element i and producing dA ionizations in a layer of thickness dx and area l cm^2. As will be shown later in Sec. 4.3.2, Q is closely related conceptually and mathematically to the photoelectric absorption coefficient for radiation. The value of Q is relatively constant for all electron energies greater than about two times the binding energy of the shell. Thus it is the increased path length for high energy electrons which increase the yield (X-ray photons produced per incident electron) rather than a change in ionization cross section.

4.1.3 Spectral continuum

Some of the incident electrons (the order of 1 part in 10^3) under go interactions in which they lose hundreds or thousands of electron volts of energy by deceleration but do not ionize the atoms. These interactions do generate X-ray photons, however, and the photons emitted in these instances form a spectral continuum. The spectral distribution rises sharply from the *Duane-Hunt short wavelength limit*, l_{min} (corresponding to the maximum incident electron energy), reaches a peak at between 1.5 and 2 times the minimum wavelength, l_{min}) and decreases slowly at longer wavelengths. This continuum spectrum is often called *Bremsstrahlung* and appears as an interfering background in the measurement of characteristic lines.

In the case of the continuum spectrum it is appropriate to speak of *spectral intensity* , I.[1,2] Subscripts λ or E may be added depending on whether the measurement is in units of wavelength or energy (for practical units see Sec. 4.4). The measured value must be corrected for detector efficiency and crystal reflectance.

4.2 X-ray generation by positive ions

Ions are similar to electrons in the way they generate X-rays except that they do not generate a measurable continuum directly. However, the electrons they eject from the atoms do generate a spectral continuum. For protons, the number of characteristic photons generated is similar to that for electrons provided that the photon energy is about 100 times greater than the electron energy.

4.3 X-ray generation by photons

The most common means of exciting characteristic X-ray photons for spectrochemical analysis by use of photon radiation from an X-ray tube to ionize the sample atoms. This photon excitation followed by photon emission is called *X-ray fluorescence*. Radiation from the X-ray tube is called the *primary radiation*; fluorescent X-rays are called *secondary radiation*. Primary radiation is generally plotted in terms of spectral intensity I_λ or I_E, or tabulated as $I_\lambda\Delta\lambda$ or $I_E\Delta E$; the tables list the number of photons in a specified $\Delta\lambda$ or ΔE interval. For a primary photon to excite characteristic emission, its energy must exceed the binding energy or ionization energy of electrons in one of the electron shells. The binding energy is designated as E_{Kabs}, E_{LIabs}, etc. The corresponding wavelength is called the characteristic *absorption edge wavelength* and is given by l_{Kabs} etc.

Two important parameters control the characteristic X-ray intensity emitted by each element in a specimen.

4.3.1 Photon emission yield (fluorescence yield).

When an outer-shell electron fills the inner-shell vacancy in an ionized atom, a characteristic photon or another outer shell electron will be emitted (such an emitted electron is called an *Auger electron*). The *fluorescence yield*, w, is the probability that the emission will be a photon. The fluorescence yield is less than 10% for low atomic-number elements but approaches unity for high atomic number elements. According to the shell originally ionized, the fluorescent yield is designated w_K, w_{LI}, etc.

4.3.2 Linear attenuation coefficient

When a beam of X-rays passes through material, the reduction in intensity per unit distance traveled is represented by the linear attenuation coefficient, μ. The attenuation is made up of two components: t the linear photoelectric *absorption coefficient* and s the *linear scattering coefficient*. For the wavelengths commonly employed in analysis (from elements $Z > 10$) t is usually more than 10 times greater than s. Ionization of atoms is related only to the t component and can be expressed in analogous fashion to the equation of Sec. 4.1.2 $dA/dx = - dq/dx = tq$ where q again represents the number of photons lost by photoelectric absorption per unit distance traveled and t replaces the Qn term in Sec. 4.1.2. Unlike Q, however, t increases approximately as l^3 or $1/E^3$ except for sharp decreases at the characteristic absorption edges (see Sec. 4.3). The ratio of the absorption coefficients on the two sides of an absorption edge is the *absorption edge jump ratio*, r.

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[1] Note: See Part I for an explanation of the use of intensity as a general term.

[2] Note: Use of the term I_θ meaning intensity measured as a function of angle is discouraged because its value is dependent on the interplanar spacing of the crystal used.

4.3.3 *Mass attenuation coefficient*, m/r. When treating X-ray transmission in multiple-component samples it is customary to use the mass attenuation coefficients, rather than the linear attenuation coefficients, μ. r is the density. For convenience, the mass attenuation coefficient of matrix element *j* for the characteristic radiation of analyte element *i*, is frequently written as μ_{ij} For a *k* component matrix *M* (including analyte element *i*) the total mass attenuation coefficient μ_{ik} is simply

$$m_{ik} = \sum_{j=1}^{k} m_{ij} c_j$$

where c_1, c_2 etc. are the concentrations of the elements expressed as fractions.

4.3.4 Secondary fluorescence.

Secondary fluorescence refers to ionization of the analyte element in a sample by characteristic radiation from other elements in the sample resulting in an enhancement of the signal measured. Secondary fluorescence is often an important contribution for elements of $Z > 20$ when the sample also contains neighboring elements of slightly higher atomic number whose characteristic photons are effective in ionizing the analyte element.

Table IV.1. Terms related to X-ray generation

Name	Practical Units	Symbol
X-ray intensity	s^{-1}	I
Relative X-ray intensity	1	I_r
Spectral intensity	s^{-1} Å^{-1}	I_l
	s^{-1} eV^{-1}	I_E
Ionization energy; Binding energy, for shell indicated	J...eV, keV	E_i; E_K, E_{LII}, E_M, etc.
Energy of emitted photon	J...eV, keV	E_{Ka}, E_{Lb}, etc.
Absorption edge wavelength	nm, Å	l_i, $l_{K\ abs}$, $l_{L\ abs}$, etc.
Wavelength of emitted photon	nm, Å	l_{Ka}, l_{Kb}, l_{La}, etc.
Absorption edge jump ratio	1	r
Cross section for ionization by electrons; for a specific electron shell	cm^2	Q; Q_K, Q_{LII}, etc.
Linear attenuation coefficient for photons	cm^{-1}	μ
Mass attenuation coefficient for photons	$cm^2\ g^{-1}$	m/r, m_{ij}, m_i
Linear photoelectric absorption coefficient	cm^{-1}	t
Linear scattering coefficient	cm^{-1}	s
Photon emission yield (fluorescence yield); for a specific shell	1	w; w_K, w_{LIII} etc.

5. TERMS RELATED TO X-RAY MEASUREMENTS

Characteristic X-rays from the different elements are distinguished either by their wavelength, l, or by their energy, *E*, depending on the type of measuring equipment employed.

5.1 Wavelength dispersion

Wavelength dispersion refers to spatial separation of characteristic X-rays according to their wavelengths.

5.1.1 Crystal diffraction.

Polychromatic radiation emitted by the specimen is limited to an approximately parallel beam by passage through a collimator (see Fig. IV.1). The beam is directed to the analyzer crystal which selectively diffracts different wavelengths at different angles according to Bragg's equation, $n\lambda = 2d \sin q$ where n is the order of diffraction,[3] d is the interplanar spacing for the diffracting planes, and q is the *Bragg angle* between the incident radiation and the diffracting planes. The angle between the diffracted radiation equal to $2q$ making the total angle between incident and diffracted radiation equal to $2q$. A grating with very fine spacing may be used instead of crystal for wavelengths greater than 1 nm but pseudo crystals of barium stearate layers etc. are preferred up to 10 nm.

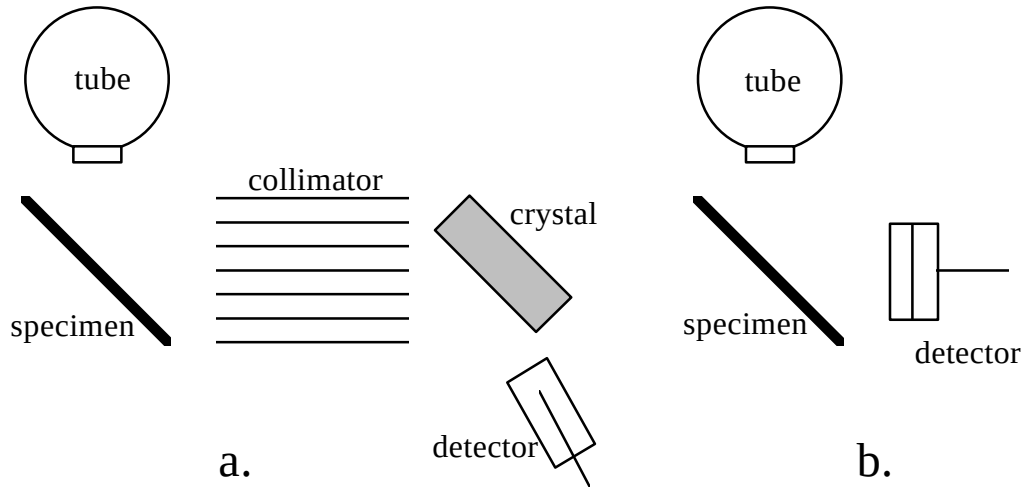

Figure IV.1. Two methods of X-ray spectrometry; a. wavelength dispersion, b. energy dispersion

By rotating the crystal, each wavelength is diffracted, in turn, up to the *maximum wavelength* $\lambda_{max} = 2d$. (The practical limit is approximately 1.8 d because of the mechanical limitations of the spectrometer.)

5.1.2 *Angular dispersion,* $dq/d\lambda$.

The change in angle q for a given change in wavelength is $dq/d\lambda = n/(2d \cos q) = \tan q/\lambda$ which means that the best separation of lines is obtained with a crystal of small d-spacing or from higher order diffraction.

5.1.3 Crystal characteristics.

The selective reflection of monochromatic radiation actually occurs over a small angular range because of crystal imperfections. The shape of the diffraction peak for monochromatic radiation is described by the *rocking curve* when the crystal is rotated through the Bragg angle. Of the incident photons which strike the crystal at angle q the fraction reflected is $P(q)$. The shape is approximately Gaussian and indicates the degree of perfection in the crystal. Three properties of the peak allow different crystals to be compared quantitatively; see Fig. IV.2. Many decades of use dictates the symbols recommended. The full width at half maximum of the rocking curve is

[3] *Note:* The use of n for order of diffraction is in agreement with recommendations of IUPAP and IUCrst but in disagreement with Part I of this series of IUPAC documents.

expressed as the *width*, W having values ranging from a few seconds of arc to ten or twenty minutes of arc. The maximum value of $P(q)$ is the *peak diffraction coefficient*, P, having values of 0.2 to 0.8 for common crystals. The *integral reflection coefficient*, R, which is $\int P(q)\mathrm{d}q$, is given in radians ($\mathrm{d}q$ is in radians) and has values ranging from 10^{-5} to 10^{-3} rad.

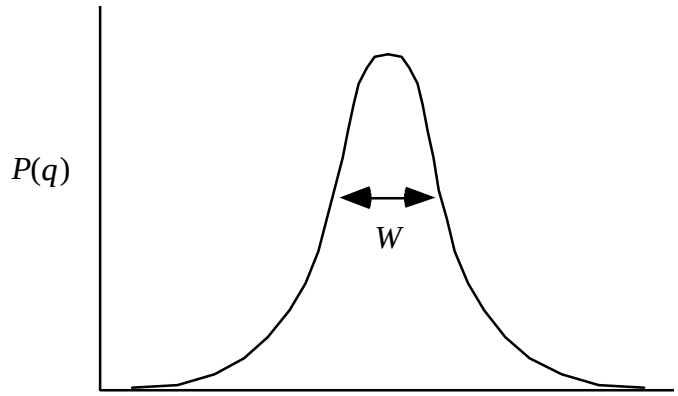

Fig. IV.2. The intensity diffracted by a crystal as a function of angle near the Bragg angle

5.1.4 Spectrometer resolution[4]

B in angular units: Referring to Fig. IV.1, the collimator allows angular divergence of the radiation passing through it. The intensity decreases linearly with angle on each side of the direct beam thus forming a triangular-shaped collimator intensity distribution at half-maximum intensity is designated as the *collimator resolution* B_C and it is convoluted (as though it were Gaussian) with the crystal rocking curve breadth, W, to give the overall spectrometer resolution, B. $B = \sqrt{B_C + W}$ B has values ranging from 10^{-3} to 5×10^{-3} rad (4 to 20 min of arc) for common collimators. Thus for a useful crystal such as LiF, (200) planes, and for 6000 eV photons, the best resolution expressed in wavelength or energy units is about 4×10^{-4} nm or less than 13 eV. Resolution degrades at higher photon energy, however, and approaches a value of 250 eV at 25.3 keV (Sn Kα). The resolution of 13 eV for 6000 eV photons should be compared with the best resolution of 135 to 150 eV for a Si(Li) detector (see Sec. 5.2.2). However, the crystal spectrometer diffracts several orders of radiation at the same q angle, i.e., if $l_2 = l_1/2$ the second order diffraction of l_2 will overlap the first order diffraction of l_1 (harmonic overlap) and they cannot be distinguished except with the aid of pulse height selection, see Sec. 5.1.5

5.1.5 Detectors for use with crystal spectrometers.

These are usually either of two types, *gas-proportional detectors* or *scintillation detectors*.

The gas proportional detector is most useful for wavelengths greater than 0.15 or 0.2 nm. It uses a chamber filled with noble gas such as Ar or Xe to absorb the X-ray photons (and a small admixture of *quench gas* such as organic vapor or a halogen to prevent re-ignition of the discharge). Absorption of an X-ray photon by the noble gas creates a number of ion-electron pairs; the number of pairs formed is proportional to the energy of the photon absorbed. A strong electric field accelerates the electrons to a central wire in the detector. In the process of acceleration, additional ionizations are produced (gas amplification) but this amplification is approximately independent of the number of initial ion pairs and the final pulse amplitude remains proportional to the photon energy. The statistical uncertainties in number of ion-electron pairs formed and gas gain result in a *pulse amplitude distribution* when photons of constant

[4] *Note:* Resolution is used differently in this document than in earlier documents of this series.

energy are absorbed. *Detector resolution*, G in eV is the full width at half maximum of this pulse amplitude distribution is given empirically by $G \approx 2.35 \sqrt{(1.7\ eE)}$ where 2.35 is the breadth at half maximum of the normal error curve; the factor 1.7 is a property of the detector and is empirically determined, e is the ionization energy, 15.8 eV for argon gas, and E is the photon energy. For 6000 eV photons, r becomes ≈ 950 eV.

After the detector absorbs an X-ray photon there is a time period known as *dead time*, t_D, during which the system is not able to respond properly to the next absorbed photon. Both the detector and the electronic amplifiers contribute to the dead time for the system; t_D may be as long as 2 µs. Dead time causes the *measured intensity* in counts per second, I_m, to be reduced below its proper value but the *corrected intensity*, I_c, can be obtained from the equation $I_c = I_m/(1 - t_D I_m)$ as long as $t_D I_m$ ² 0.1.

The scintillation detector is generally used for wavelengths shorter than 0.2 nm. The detector consists of a crystal such as NaI activated with Tl so that visible emission occurs when an X-ray photon is absorbed. A photomultiplier coupled to the crystal amplifies the emission and produces an electrical pulse proportional to the X-ray photon energy.

The scintillation detector has a G about three times larger than that of the gas-proportional detector for the same photon energy; the dead time is similar to that for the gas-proportional detector.

5.2 Energy dispersion.

Energy dispersion refers to the separation of characteristic photons according to their energy. No crystal spectrometer is required (see Fig. 1b), but, to be practical, the detector must have better energy resolution than the gas-proportional or scintillation detectors used in wavelength dispersion.

5.2.1 Solid-state detector.

The most common *solid-state detector* is Si(Li); it consists of a disk of Si which is suitably doped and with Li diffused into the central region. A reverse-bias potential is applied across the surfaces. When an X-ray photon is absorbed in the central region it produces a number of electron-hole pairs proportional to the energy of the absorbed photon. These electrons and holes are attracted to the opposite surfaces and constitute an electrical pulse.

In Si(Li) detector circuits t_D is much larger than in Sec. 5.1.5 due to processing and storage requirements for each pulse, but the correction to obtain I_c is made electronically by the timing circuit which measures time only when the circuit is able to accept a pulse. However, other factors such as rapid accumulation of pulses in the preamplifier limit the counting rate to about 20 000 counts per second.

5.2.2 Resolution of Si(Li) detectors.

Because of defects, impurities and other loss mechanisms the number of electron-hole pairs shows some statistical variation for constant photon energy. This amounts to broadening the pulse amplitude distribution of the characteristic X-ray photons and can be expressed in terms of energy resolution. The equation for the statistical contribution, G(s). to the full width at half maximum of the pulse amplitude distribution, is given by the relationship $G(s) \approx 2.35 \sqrt{(F\ e\ E)}$ where F is a dimensionless factor, the Fano factor, whose value is estimated to be between 0.1 and 0.13 for Si(Li), E is the photon energy in eV. For a photon energy of 6000 eV the value of G(s)would be about 125 eV.

Noise, primarily in the pre amplifier and to some extent in the detector, adds a contribution of about 80 eV which can be added quadratically to G(s) and increases the observed G to $\approx \sqrt{(125^2 + 80^2)} \approx 150$ eV. This resolution is sufficient to separate the Ka lines of neighboring elements but not sufficient to resolve the Kb line of element Z from the Ka line of element $Z + 1$ in the atomic number region from $Z = 16$ (S) to $Z = 27$ (Co). The resolution of 150 eV for the solid-state detector is far better than the 950 eV resolution of the gas-proportional detector (Sec. 5.1.1) but far poorer than the 13 eV resolution of the crystal spectrometer (Sec. 5.1.4).

5.2.3 Multichannel analyzer.

In energy-dispersion X-ray analysis the *multichannel analyzer* is an instrument used to store information from the Si(Li) detector. Each channel (memory cell) corresponds to a small energy increment, ΔE. Each pulse from the detector is stored in the appropriate channel according to the amplitude of the pulse (ergo, the photon energy). The stored information in the multichannel analyzer is the spectral intensity as a function of energy $I_E \Delta E$, for the absorbed radiation discussed in Sec. 4.1.3.

5.3 Terms related to X-ray measurement

Name	Practical Units	Symbol
Energy per electron hole pair or per electron	eV	e
Fano factor	1	F
Resolution of detector or spectrometer	eV or nm	G
Bragg angle for crystal diffraction	rad, deg	q
Spacing between crystal diffracting planes	nm, Å	d
Wavelength	nm, Å	l
Crystal rocking curve width	rad, deg	W
Peak diffraction coefficient	1	P
Integral reflection coefficient	rad	R
Angular dispersion	rad/nm or rad/Å	$\mathrm{d}q/\mathrm{d}l$
Detector dead-time	s	t_D

6. TERMS RELATED TO X-RAY DATA INTERPRETATION AND QUANTITATIVE ANALYSIS

6.1 Measuring relative X-ray intensity,

Whatever the means of separating the characteristic lines of the elements contained in the specimen, it remains to measure the X-ray intensity of one emission line for each element in order to relate it to composition. The general procedure is to use relative X-ray intensity as the measured parameter. In order to obtain the relative intensity it is necessary to correct for the dead time (see Sec. 5.1.5) and for the interfering background (see Sec. 4.1.3 and 6.2 following).

6.2 Counting precision

For X-ray measurements *counting precision* is very easy to estimate because the photons are counted individually and photon emission is a random-time process for which a Poisson distribution can be assumed. Therefore, the *standard deviation for counting*, $s(N)$, for a single

measurement of N counts where N is large is simply $s(N) = \sqrt{N} = \sqrt{It}$ where I is the intensity in counts per second and t is the counting interval in seconds. The rules for adding variance apply to the effects of other random errors introduced by subtracting background or taking ratios of intensities. For example, when the signal N_p in total counts at the line-peak position and N_B at the background position are both measured, the value of $s(N)$ for the characteristic line above background becomes $s(N) = \sqrt{(N_p + N_B)} = \sqrt{((I_p + I_B)t)}$. Inasmuch as N_p and N_B are usually large numbers (greater than 1000) the standard deviation for a single measurement is a good approximation of the true standard deviation, s (see Part II). The *relative standard deviation*, s_r can be written as $s_r = \sqrt{(N_p + N_B)} /(N_p - N_B)$

6.3 Analytical curves

One method of quantitative X-ray spectroscopy makes use of reference samples of known composition to prepare analytical curves relating X-ray intensity to concentration for each analyte element (see Part II concerning terminology for sensitivity S and limit of detection c_L). For multicomponent samples a family of analytical curves may be needed for a single analyte because of variations in the balance of other elements. This makes the analytical curve approach of limited usefulness and encourages the use of more powerful data interpretation schemes.

6.4 Analytical functions

Analytical functions with empirical coefficients: as is stated in II 3.2, the measure x_i of element i in a specimen can be expressed as a general function of concentrations of all elements present

$$x_i = g_i(c_1, c_2, c_3, \ldots c_n) \quad \text{Eqn. IV.1}$$

For X-ray spectroscopy a useful form of the analytical function is the regression equation:

$$c_i / I_{r,i} = a_{i0} + \sum_{j=1}^{n} a_{ij} c_j \quad \text{Eqn. IV.2}$$

where $I_{r,i}$ is the measured relative X-ray *intensity* for element i, a_{i0} is the intercept on the $c_i/I_{r,i}$ axis, $a_{ii} + a_{i0} \equiv 1$ and the other a_{ij} values are empirically determined influence coefficients representing the effect of element j on element i. Numerical values for a_{ij} are obtained by measuring a series of reference samples of known composition and solving for the a values in the set of simultaneous equations represented by Eqn IV.2.

The particular form of Eqn IV.2 has several distinct advantages over other forms of regression equations: first, it is nonlinear in $I_{r,i}$ which allows a better approximation to realistic analytical curves; second, the curved line which results for a local range of c_i is not constrained to pass through the origin (because of the a_{i0} term); third, it is easy to solve for the a's because when $I_{r,i}$ and the c's are known for reference samples, the equations are linear for the a's; and fourth, the equations are linear in evaluating an unknown because the values of $I_{r,i}$ are measured and hence constant for each equation.

6.5 Fundamental-parameter equations

Fundamental physical parameters may be used to calculate the intensity vs. concentration relation without recourse to empirical coefficients. The fundamental parameters required are spectral intensity of the primary radiation (Sec. 4.1.3), the mass attenuation coefficients (Sec. 4.3.3), the photon emission yield for the specific line (Sec. 4.3.1) and the fraction absorption by each electron shell (the jump ratio). The equations that are used contain summations over all incident wavelengths and all depths in the sample and treat primary excitation separately from

enhancement. Such equations require computer evaluation but allow maximum versatility in analysis.

6.6 Terms Used in Data Treatment and Analysis

Name	Practical Units	Symbol
Total number of events at position of line peak or background position	1	N_p, N_B
Relative standard deviation	1	s_r
Influence coefficient for the effect on element i by the presence of element j	1	a_{ij}
Standard deviation for counting	counts	$s(N)$