SENSITIVITY, SPECTRAL-LINE INTERFERENCE, ABSORPTION-ENHANCEMENT EFFECTS AND COUNTING STATISTICS

3.1 X-Ray Spectrometry Systems

3.1.1 Introduction

An x-ray spectrometry system is a device for converting x-ray intensity into concentration. It consists of:
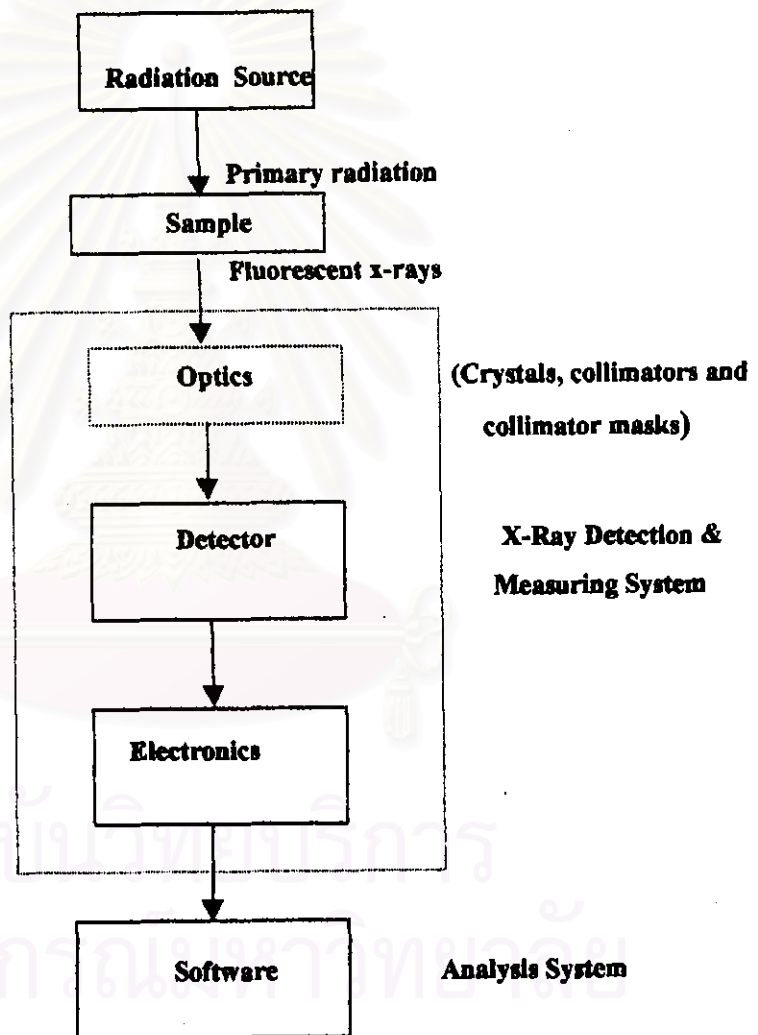

Figure 3.1 The X-Ray Spectrometer Schematic System

-A source of exciting radiation (for example: X-rays, γ-rays, electrons, protons, etc.) .

-A sample handling and presentation system.

-A spectrometer, i.e. a means of dispersing (separating) the excited sample spectrum (e.g. crystals, detectors, filters) into its component wavelengths or energies.

-A system for detecting and measuring the intensity of the x-rays at a selected wavelength or energy (e.g. gas counter, solid state detector, scintillation counter).

-It usually includes a computer for converting the raw data into meaningful information (normally concentration values per element).

The spectrometer is based on one of two following principles: It may be energy-dispersive or wavelength-dispersive .

a.   Energy Dispersive Spectrometers (EDS) rely on the energy resolution of the detector, and the proportionality of the detector output pulse voltage with energy of the x-ray photon producing that pulse. Most EDS systems use multi-channel analyzer, where the channel number is proportional to the voltage of the detector pulse. The concentration of an element in the sample is, to a first approximation, proportional to the intensity at a selected energy.

b.   Wavelength Dispersive Spectrometers (WDS) use single crystal (or multi-layers) of a suitable material to disperse the spectrum according to Bragg's law. Each characteristic line has a discrete wavelength and therefore a discrete Bragg angle (θ). For the determination of an element, this angle is either set on a scanning goniometer, or established during the manufacture of a "fixed" channel. The concentration of an element in the sample is, to a first approximation, proportional to the intensity at the selected wavelength

3.1.2   Energy Dispersive Spectrometers (EDS)

Energy Dispersive X-ray Spectrometry (EDXRF) relies solely on the property of most x-ray detectors that the output pulse size is proportional to the energy of the x-ray photon that produced it. If the size of the output pulse is measured, this reveals the energy (and therefore also wavelength) of the x-ray photon.

The most commonly used detector in EDXRF systems is the solid state Si(Li) detector. The energy resolution of this detector varies slightly with energy, is usually quoted at around 150 eV (Full Width at Half Maximum) at the Mn K_α energy (5.9 keV).

In order to achieve this resolution, the detector must be operated at a very low temperature (liquid nitrogen ~ 77°K) to reduce the "noise" component, and all

spectrometers with this type of detector are fitted with a liquid nitrogen reservoir and a cold finger. When a x-ray photon is stopped in the detector, a cloud of ionization is produced in the form of electron-hole pairs. All of the x-ray photon's energy is released in this process and the number of electron-hole pairs generated is proportional to the energy of the incoming photon. The pulses produced by the Si(Li) detector are amplified and fed to a multi-channel analyzer (MCA) the purpose of which is to measure the size of each pulse, and represent this size as an integer (channel) number. Thus all pulses are counted and assigned a channel number which is a direct measure of x-ray photon energy. The spectrum can then be displayed with intensity on the Y-axis and photon energy on the X-axis.

The excitation source in an EDX spectrometer can be either an x-ray tube, or a radioactive source, e.g. ^{241}Am.

For reasons of cost and simplicity, other detectors such as the gas-filled proportional counters or the scintillation detectors are sometimes used, but their poorer resolution (~1200 and 3000 eV, respectively, at Mn K_α) limits general use. They find use in simpler applications where resolution are not the prime requirement.
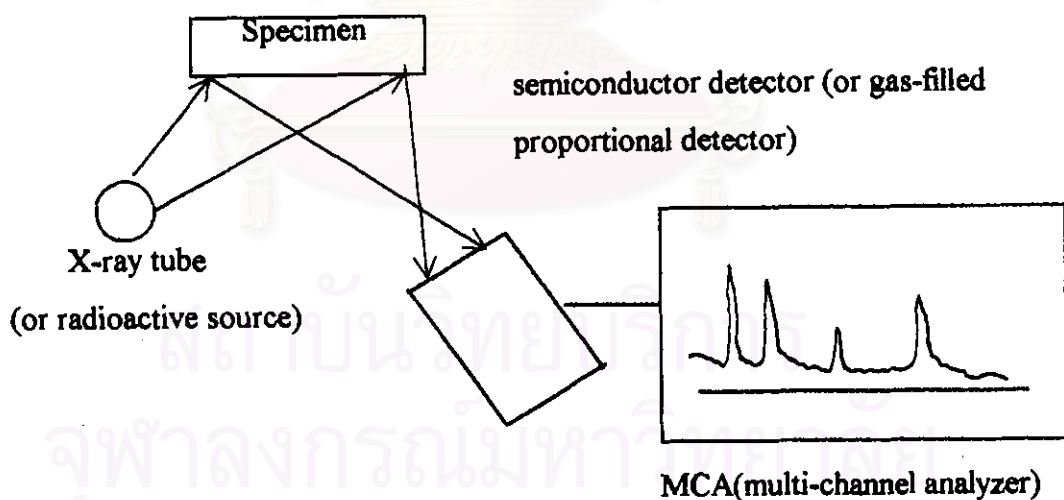

Figure 3.2 Energy Dispersive Spectrometer (EDS)

Gas-filled proportional counters use a conventional pulse height selector to isolate the spectral line of interest from the unwanted radiation (other lines and scattered background). Since the resolution of these detectors is relatively poor (~3000 eV for Mn K_α), applications of this type of spectrometer must be simple.

Advantages of EDXRF

The most common use of EDXRF is rapid qualitative analysis of unknown specimens, but quantitative analysis is not uncommon. When a Si(Li) detector is used the whole spectrum of the sample can be collected, adequately dispersed, and displayed simultaneously. Of course, its analytical sensitivity is worse than that of WDXRF. Due to its general suitability for qualitative analysis, the EDX spectrometers can be used for very large pieces to be presented, and therefore useful to test antiques and archaeological artefacts such as jewellery , paintings, whole pieces of pottery and earthenware. This is the main advantage of EDXRF. Morever, Energy Dispersive systems are relatively inexpensive, when compared with a WDXRF system.

Disadvantage of EDXRF

- The spectral resolution for the lighter elements (Z<20) is considerably worse than for WDXRF (Resolutions of EDXRF and WDXRF are 150eV and 20eV, respectively, at 1.25KeV Mg K_α). Severe spectral overlaping for the elements Na, Mg, Al, and Si makes their determination in oxide mixture such as rocks, ceramics and minerals difficult and potentially inaccurate.

- Because of the adverse effect that high counting rates have on detector resolution, and because of the inherent high dead time of the system, total countrates for Si(Li) detector used systems are limited to about 20,000 cps. Hence, in the samples where a major element predominates the sensitivity for the other elements is considerably low.

- The need for liquid nitrogen to cool the Si(Li) detector leads to high cost. In recent years, attempts to produce a room temperature solid state detector with acceptably low electronic noise have been reasonably successful, and the so-called Peltier cooled detector has found application particularly in x-ray diffraction systems.

3.1.3 Wavelength dispersive X-ray spectrometer

The principle of wavelength dispersion is based on Bragg's diffraction phenomenon that is mentioned in chapter 1. Single crystal or atomic multi-layers, either naturally grown, or synthetically produced, are used to diffract on-line the polychromatic beam of X-rays from the sample. By selecting the relevant Bragg angle (θ), then an individual wavelength (spectral line of an element) which satisfied the Bragg's law

$$n\lambda = 2d\sin\theta \qquad\qquad (3\text{-}1),$$

where λ is wavelength of the spectral line,

      d is the interplanar spacing of the crystalline material,

      n is order of reflection.

may be measured, and therefore, X-ray spectra are relatively simple, often without interference from any other line. As a consequence, the analytical sensitivity and resolution of WDX spectrometer are often high for all elements.

The dispersion of the spectrum by the crystal can be derived by differentiating the Bragg equation (3-1), i.e.

$$d\theta \,/d\lambda \;=\; n\,/\,2d\,\cos\theta \qquad\qquad (3\text{-}2),$$

From this equation it can be seen that dispersion increases with decreasing $\cos\theta$ (increasing θ), and with decreasing value of 2d. In addition, the higher the order of the reflection (n), the better the dispersion. The resolution of the system is governed by the natural width of the spectral line, the "rocking angle" of the crystal, and the solid angles of acceptance of collimators or slits. It is clear from the above equation that resolution will be particularly poor at low angles, the relative wavelength separation of the spectral lines of neighboring atomic numbers decreases with θ for a fixed value of d.

The most popular type of WDXRF spectrometer is the sequential or scanning type. This type of the spectrometer is the most versatile, and is normally fitted with up to three primary collimators, up to eight analyzing crystals, and two or three different detectors, so that all elements (Z = 4 to 92) may be determined, and optimum parameters may be set for each sample type and for each element. Because of its scanning nature the sequential spectrometer is capable of both qualitative, semi-quantitative and quantitative analysis.
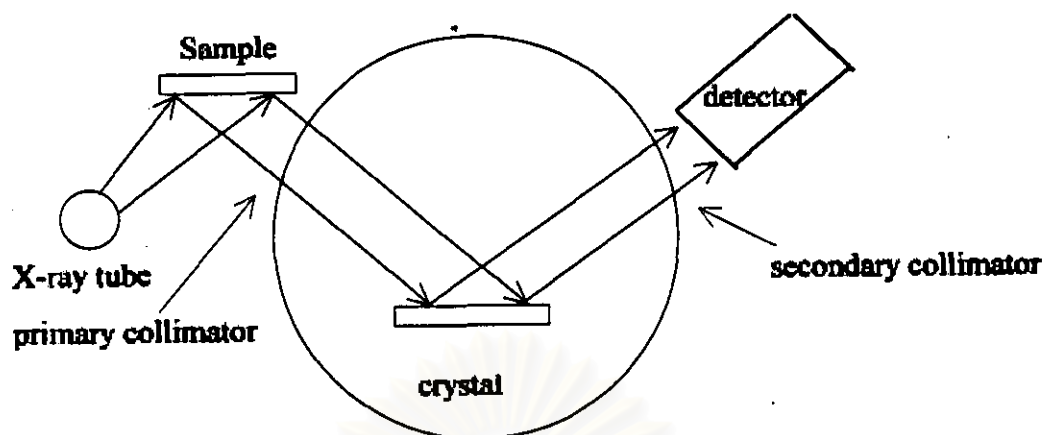
. **Figure 3.3 WD Sequential Spectrometer**

Some other differences between wavelength-dispersive (WD) and energy-dispersive (ED) XREF that should be noted are:

1. The brightness of a WD spectrometer is very low, the crystal is responsible for an important part of the losses. This problem may be overcome by the use of radiation source of significant intensity.

2. The crystal is the dispersive device only, not the detecting device. The situation is different in EDXRF, where it plays a double role, as the dispersive device and as the detector at the same time.

3. Since Bragg's law is of geometric character, the conditions for the collimation of primary and secondary beams are very severe for WDXRF device, not the same as for EDXRF.

4. An attractive aspect of EDXRF is the simultaneous collection of the whole spectrum, the action of a typical WDXRF device is exclusively sequential. The maximum count rate for an EDXRF instrument, however, is about 20,000 cps for the whole spectrum, which severely limits the total number of accumulated counts and consequently limits the precision (counting statistics). Simultaneous WD instruments are composed of a series of individual crystal spectrometers (channels) operating simultaneously, but the number of channels is limited.

3.2 Sensitivity

Sensitivity in x-ray spectrometric analysis may be defined in either of two ways - in terms of minimum detectable amount of analyte, or rate of change of analyte-line intensity with change in amount of analyte.

The minimum detectable amount, or limit of detectability is the amount of analyte that gives a net line intensity equal to three times the square root of the background intensity, or in statistical terms, the amount that gives a net intensity equal to three times the standard counting error of the background intensity. "Amount" signifies concentration (%, mg/ml, etc) for infinitely thick specimens, area density (mg/cm^2) for specimens less than infinitely thick, or mass (μg) for extremely small particulate or filamentary specimens.

3.3 Factors affecting sensitivity

Sensitivity is usually improved by increasing analyte-line intensity. Analyte-line intensity may be increased by the following conditions:

3.3.1 Excitation conditions

1. X-ray tube potential and current is as high as possible. However, background may also increase with x-ray tube potential and current. So, in some cases it may be preferable to reduce excitation to increase line-to-background ratio.

2. X-ray tube target atomic number is as high as possible to give high continuum intensity.

3. X-ray tube window of beryllium is as thin as possible, especially when low-Z analytes are to be determined.

4. X-ray tube target-to-window distance is as small as possible so that the target-to-specimen can be made small.

5. Primary beam filters should be avoided because such filters always reduce primary beam intensity, and therefore analyte-line. However, in some cases the filters may improve line-to-background ratio, and thereby decrease the detectable limit.

6. Irradiated area on the specimen plane is as large as possible.

3.3.2 Specimen conditions

1. Useful specimen area is equal to or greater than the area of the projection of the spectrometer optical system on the specimen plane.

2. Analyte absorption-edge wavelength is just longer than the wavelengths of the excitation source.

3. Matrix absorption coefficient is low.

4. Matrix spectral lines enhance the analyte line.

5. Dilution should be used for a matrix having high absorption coefficient.

6. Preconcentration or separation of analyte of low concentration should be made.

7. Particle size of powder or briquet or surface texture of solid specimens is less than 50 - 100 μm.

8. Optimal analyte-line should be used, for example with a 50KV generator, in practice K-lines are always used for elements up to atomic number 40 (Zirconium), and L-lines are always used above atomic number 60 (Neodymium). However, sometimes an L-line, although less intense than a K-line, may give a more favorable line-to-background ratio if it occurs in a less intense region of the scattered continuum.

3.4 Spectral-line interference

3.4.1 Definition

There are two types of x-ray spectral-line interference: (1) wavelength (2θ) interference, in which the interfering line overlaps the 2θ interval occupied by the analyte-line; the interfering and analyte lines may have the same or nearly the same wavelength (λ) or product of order and wavelength ($n\lambda$); and (2) energy interference, in which the interfering pulse-height distribution overlaps the analyte pulse-height distribution.

Thus, spectral interference may be defined as that condition whereby (1) photon of a line other than the measured line enters the detector at the 2θ angle of the measured line, and/or (2) pulses caused by a line other than the measured line enter the window of the pulse height analyzer at the setting for the measured pulse height distribution.

3.4.2 Common sources of spectral interference

The great majority of instances of spectral-line interference may be classified in one of the following four categories, regardless of the source of the interfering line:

1. Superposition of first-order lines of the same series (K, L, M) from adjacent or neighboring elements in the periodic table. For example the K_α lines of adjacent elements above technetium (Z=43) lie within 0.03 A of one another, as do the $L_{\alpha 1}$ lines of adjacent elements above mercury (Z=80).

2. Superposition of first-order lines of different series; for example As K_α (λ=1.177 A) and Pb $L_{\alpha1}$ (λ=1.175 Å).

3. Superposition of first-order K-lines and higher order lines from elements of higher atomic number, for example Ni K_α (λ=1.659 Å) and Y K_α (2λ=1.660 Å). This type of interference is particularly troublesome in the determination of low-Z elements in multicomponent samples having many medium-Z and high-Z elements.

4. Superposition of first-order L-lines and higher-order K-lines from elements of lower atomic number. For example Hf $L_{\alpha1}$(λ=1.570 Å) and Zr K_α (2λ=1.574 Å); Ta $L_{\alpha1}$(λ=1.522 Å) and Nb K_α(2λ=1.494 Å).

Similar interferences also exist between $L_{\beta1}$ and second-order K_β-lines of these elements.

3.4.3 Reduction of spectral interference

The methods for reduction of spectral interference may be classified in nine categories as follow:

1. Selection of an alternative analyte-line that is free from interference.

2. Removal or reduction of the concentration of the interfering element

3. Prevention or reduction of the efficiency of excitation of the interfering element or increase of the efficiency of excitation of the analyte.

4. Increase of the resolution of the spectrometer.

5. Prevention or reduction of the transmission of the interfering line through the spectrometer, or increase of the transmission of the analyte-line.

6. Prevention or reduction of the efficiency of detection of the interfering line, or increase of the efficiency of detection of the analyte-line.

7. Prevention of the counting of detector pulse originating from the interfering line.

8. Correction for the interfering line by experimental technique.

9. Correction for the interfering line by mathematical means.

The practicability of any approach to the reduction of spectral interference is determined by the specific features of the particular case such as the relative intensities of the analyte-line and interfering line, the degree of their overlaping, and the difference in their true wavelengths (λ, not $n\lambda$) determine the seriousness of the interference.

3.5 Absorption-enhancement effects

The effects of the matrix on analyte-line intensity can arise from the following phenomena:

1. The matrix absorbs primary x-rays: its mass absorption coefficient may be larger or smaller than that of the analyte for primary x-rays and it may preferentially absorb or transmit those wavelengths that excite the analyte-line most efficiently. That is, those near the short wavelength side of the analyte absorption edge.

2. The matrix absorbs the secondary analyte-line radiation: its mass absorption coefficient may be larger or smaller than that of the analyte for the analyte-line radiation, and it may preferentially absorb or transmit this wavelength.

3. The matrix elements emit their own characteristic lines which may lie on the short wavelength side of the analyte absorption edge, and thereby excite the analyte to emit additional line radiation. This is called the enhancement effect. For example as stainless steel (Cr-Fe-Ni system): Fe (K_{ab}=7.111 KeV) can be excited by Ni $K_{\alpha 1}$ (=7.477 KeV)

The absorption-enhancement effects dealt with here are nonspecific (general) and specific. Nonspecific or general absorption-enhancement effects result simply from differences in the absorption coefficients of analyte and matrix elements for the primary x-rays and especially for analyte line radiation. Nonspecific effects can often be evaluated by simple calculations based on the absorption coefficients of analyte and matrix elements.

Specific absorption-enhancement effects result from interactions of analyte and matrix spectral lines and absorption edges in close proximity. They are evaluated by measurement of analyte line intensity from mixtures of the analyte and a single matrix element in various proportions. The more complex secondary effects are evaluated by measurement of analyte line intensity from a specific analyte-matrix element pair as the remainder of the matrix is varied.

3.5.1 Nonspecific absorption effect

Figure 3.4 shows a series of calibration curves that illustrate nonspecific absorption effects and apparent enhancement effects. The curves represent various combinations of analyte and matrix absorption coefficients for the analyte-line and for the primary radiation that excites the analyte most efficiently. μ/ρ represents the total mass-absorption coefficient for both primary and analyte line radiation.
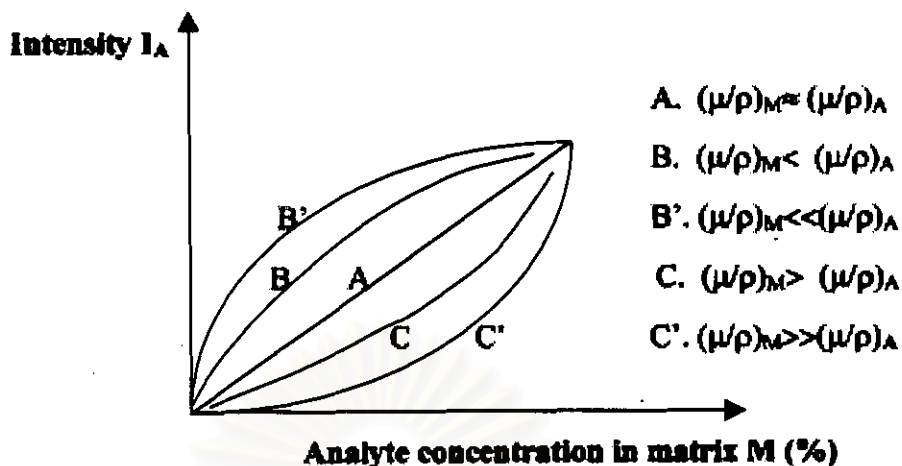
Figure 3. 4 Absorption-enhancement effects

In a neutral matrix (curve A) the absorption coefficients of the matrix $(\mu/\rho)_M$ and analyte $(\mu/\rho)_A$ are substantially the same for both the analyte line and the primary radiation that excites the analyte most efficiently. The primary x-rays reach each incremental specimen volume and the excited analyte line radiation emerges from the specimen with about the same attenuation in the matrix as well as in the pure analyte. Thus, analyte line intensity I_A increases at about the same rate as concentration C_A. The I_A - C_A curve is substantially linear and the absorption effect is very small.

In a light matrix (curves B and B'), $(\mu/\rho)_M$ is less than $(\mu/\rho)_A$ for the analyte line and primary x-rays. In such a matrix, the primary x-rays undergo less attenuation in reaching any incremental specimen volume and analyte line radiation undergoes less attenuation in emerging from the specimen in the matrix than in the pure analyte. Thus, I_A increases at a faster rate than C_A. At very high concentrations, this means that the specimen composition approaches the pure analyte, then the difference in rates of increase for I_A and C_A decreases. The I_A - C_A curves are nonlinear and show the positive absorption effect which constitutes an apparent enhancement effect.

In a heavy matrix (curves C and C'), $(\mu_A/\rho)_M$ is greater than $(\mu/\rho)_A$, primary and analyte line radiation undergo greater attenuation in the matrix than in the pure analyte, so I_A increases at a slower rate than C_A and the curves show the negative absorption effect.

3.5.2 Specific absorption-enhancement effects

If the analyte line A occurs at a wavelength just less than that of an absorption edge of a particular matrix element B, The A line is strongly absorbed by the element B and it's intensity is reduced in proportion to concentration of element B. For example as case of Fe K_α(1.94 A) in the presence of chromium (K_{ab}=2.07 A), and chromium has a similar, but progressively weaker, negative absorption effect on the K_α lines of elements of successively higher atomic number - Cobalt, Nickel, Copper, etc.

Conversely, If the A-analyte absorption edge occurs at a wavelength just greater than that of a line of a particular matrix element B, The B-line is absorbed by A, and A-line intensity is enhanced in proportion of concentration of the element B. For example as case of Fe K_{ab} (1.74 A) and Ni K_α (1.66 A), and Nickel has a similar, but progressively weaker, enhancement effect on the K_α lines of elements of successively lower atomic number - Manganese, Chromium, Vanadium, etc.

The effects just described are specific and depend on the proximity of spectral lines and absorption edges of analyte and matrix elements.

3.6 Counting statistics

3.6.1 Counting error for accumulated counts

1. Single measurement

For a single measurement of N counts, standard deviation (or standard counting error) σ_N and relative standard deviation ε_N are given by:

$$\sigma_N = \sqrt{N} \tag{3-3},$$

$$\text{and} \quad \varepsilon_N = \sigma_N/N = 1/\sqrt{N} \tag{3-4};$$

2. Net intensity

Let us call N_p is total counts at the analyte peak;

and N_b is counts of background measurement.

If both measurements are taken for the same time interval, then net intensity at the peak of interest is:

$$N = N_p - N_b \tag{3-5};$$

its standard deviation:

$$\sigma_N = (\sigma_p^2 - \sigma_b^2) = (N_p + N_b)^{1/2} \tag{3-6};$$

and relative standard deviation:

$$\varepsilon_N = \sigma_N/N = (N_p + N_b)^{1/2}/(N_p - N_b) \qquad (3\text{-}7);$$

It is evident that standard counting error decreases as N increases, and in principle, it may be made as small as required if a sufficiently long counting time is permissible. However, accumulation of a large count at low intensity requires a very long counting time, this may be disadvantageous for several reasons: (1) Analysis time is increases, (2) Extremely high stability is required in the x-ray tube potential and current and in the detector and electronic equipment accompanied.

3.6.2 Counting error for count rate

1. Uncorrected count rate

If N is total counts at the analyte peak in a measuring time T,

then count rate I=N/T (cpm or cps) ;

Standard counting error is given by:

$$\sigma_I^2 = (\partial_I/\partial_N)^2 \sigma_N^2 = N/T^2 = I/T$$

$$\Rightarrow \qquad \sigma_I = (I/T)^{1/2} \qquad (3\text{-}8);$$

and relative counting error is:

$$\varepsilon_I = \sigma_I/I = (1/IT)^{1/2} = 1/\sqrt{N} = \varepsilon_N \qquad (3\text{-}9);$$

That is, $\sigma_I/I = \sigma_N/N$ $\qquad (3\text{-}10);$

2. Net count rate

If Ip and Ib are count rates at the analyte peak and background, respectively;

net count rate $I = I_p - I_b$ $\qquad (3\text{-}11);$

from (3-8) we have:

$$\sigma_{Ip} = (I_p/T_p)^{1/2} \text{ and } \sigma_{Ib} = (I_b/T_b)^{1/2}; \qquad (3\text{-}12);$$

where T_p and T_b are the counting times for the peak and background, respectively.

Then, $\sigma_I = (\sigma_p^2 + \sigma_b^2)^{1/2} = (I_p/T_p + I_b/T_b)^{1/2}$ $\qquad (3\text{-}13);$

and $\varepsilon_I = \sigma_I/I = (I_p/T_p + I_b/T_b)^{1/2}/(I_p - I_b)$ $\qquad (3\text{-}14);$

These quantities of error are needed for experimental data processing as well as for accessing accurate level of obtained analyte concentration in the chapter 5 of the thesis.

3.7 Detection limit

A characteristic line intensity decreases with decreasing concentration of the analyte and finally disappears in the background noise. If the measured analyte-line intensity I_p is larger than background, we assume the analyte to be present. if the

measurements follow a Gaussian distribution and $I_p = I_b + 2\sigma_b$, then the probability that the analyte is present is approximately 95%. If $I_p = I_b + 3\sigma_b$, the probability is 99.7%, in this case, the net intensity is thus $3\sigma_b$ and the detection limit (DL) is:

$$DL = 3\sigma_b / M \qquad\qquad (3\text{-}15),$$

where M is the sensitivity in counts per second per percent. In x-ray spectrometry, however, the background is sample dependent and can not measured independently as in radioactivity measurements. Hence I_b must be measured in an off-peak location in the spectrum and two measurements must be made: I_p and I_b. The detection limit thus becomes:

$$DL = [3\sqrt{(I_b / T_b)}] / M \qquad\qquad (3\text{-}16),$$

It is obvious that the detection limit decreases if the counting time increases. However, the total error in I_b contains the instrumental error as well. There is thus no sense increasing the counting time when the instrumental error dominates.