Quantitative XRD & XRF Analyses — Unified & Simplified

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Abstract

Bothered by the complex matrix effects, the current practice of quantitative XRD & XRF analyses require Intensity-Concentration calibration lines from standards, which is tedious and time-consuming. New insights led to the three laws of quantitative XRD & XRF analyses: 1. the law of zero matrix effects, 2. the law of constant slope of calibration lines, and 3. the law of binary mixtures. The first two laws change the current concept of quantitative XRD & XRF analyses. The third law unifies and simplifies the quantitative XRD & XRF analyses. Consequently, one decoding formula quantifies both XRD & XRF. Just one X-ray scan of one sample preparation determines all compounds (XRD) or elements (XRF) in any mixtures. This new procedure reduces lab work by some 80% required by current practice, with a statistical precision of ± 5% or better.

Keywords

X-ray diffraction, X-ray fluorescence, X-ray spectrometry, powder diffraction, matrix effect, adiabatic principle, specific intensity

1. Introduction

All current textbooks on quantitative X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses teach the Internal Standard and/or the Spiking methods. Both methods require calibration lines from standards, which is tedious and time-consuming. New insights lead to three laws of quantitative XRD & XRF analyses: 1. the law of zero matrix effects; 2. the law of constant slope; and 3. the law of binary mixtures. These three laws transform any complex mixture into a set of simple binary mixtures. Moreover, one of the two components in each binary mixture has known % weight. The % weight of the other component is obvious. These three laws unify and grossly simplify the quantitative XRD and XRF analyses of mixtures.

2. Unified theory of quantitative XRD & XRF

Examine the fundamental equations relating intensity (I_i) to concentration (X_i), (Klug & Alexander, 1974; Herglotz & Birks, 1978; Jenkins et al., 2002; Grieken & Markowicz, 2002), we found that with a fixed experimental setup, the fundamental intensity-concentration equations of both XRD & XRF becomes $I_i = k_i X_i$, where k_i is an overall constant including the absorption coefficient (μ), density (ϱ), thickness (d) of the specimen and other instrumental parameters. Note that the μ & ϱ factors vary with the composition and the d factor varies with specimen preparation. However, all components in the same specimen have identical μ, ϱ & d factors, which can be exactly cancelled mathematically.

- According to Klug and Alexander (1974) for XRD with pellet specimen:

$I_i = K_i X_i / \mu = k_i X_i$ Where K_i is a proportional constant, k_i includes K_i / μ factor. (1)

- According to Herglotz & Birks (1978) for XRF:

$I_i = K_i X_i (1 - e^{-\mu \varrho d}) / \mu = k_i X_i$ Where k_i includes $K_i (1 - e^{-\mu \varrho d}) / \mu$ factor (2)

With pellet specimen, where $d = \infty$, $e^{-\mu \varrho d} = 0$, we have (Chung, 2016):

$I_i = K_i X_i / \mu = k_i X_i$ Where k_i includes the K_i / μ factor. (3)

With thin-film specimen (Chung et al., 1974), for which d is very small. We have

$e^{-\mu \varrho d} = 1 - \mu \varrho d$

$I_i = K_i X_i \varrho d = k_i X_i$ Where k_i includes the $K_i \varrho d$ factors. (4)

Bundling the K_i and the μ, ϱ & d factors into an overall constant (k_i) creates six effects: 1. Leave the μ, ϱ & d factors out of the decoding formula. 2. Cancel the μ, ϱ & d factors in the k_i/k_s ratios. 3. Make the k_i factor a characteristic constant (i.e. constant slope of calibration line) of each component sought. 4. One simple equation decodes both XRD & XRF, 5. It works for full range of concentrations, and 6. No restriction on the amount of reference standard (X_s). Note that in the Internal Standard method, all samples must have identical X_s (Klug and Alexander, 2nd Ed. P. 537, 1974), which is very tedious.

Let us implant known amount of a reference standard (X_s) into the totally unknown mixture and homogenize the admixture. Couple the reference standard (s) with each of the original components (i). Now we have a pair of simultaneous equations for each original component. Note that each component in the same specimen has identical μ, ϱ, & d factors, hence these matrix factors are neatly cancelled in the ratio k_i / k_s in Equations (5) & (6) for both XRD & XRF.

$I_i = k_i X_i$ and $I_s = k_s X_s$

$$\frac{I_i}{I_s} = \frac{k_i}{k_s} \bullet \frac{X_i}{X_s}, \quad k_s = 1.00 \text{ by definition (see section on Specific Intensity)}$$

$$\frac{I_i}{I_s} = k_i \bullet \frac{X_i}{X_s}, \quad k_i = \text{slope of a straight line.} \qquad (5)$$

Rearrange Equation (5), we have:

$$X_i = \frac{X_s}{k_i} \bullet \frac{I_i}{I_s} \quad \text{The basic decoding formula.} \tag{6}$$

Note that each individual k_i and k_s contains matrix factors (μ, ϱ & d). However, the ratio k_i / k_s is free from matrix factors, because all matrix factors (μ, ϱ & d) are exactly cancelled.

Equations (5) & (6) indicate k_i = slope of calibration line = characteristic constant of component i. Consequently, the complex matrix factors and the tedious calibration work are eliminated. Equation (6) is the new basic decoding formula for both XRD & XRF. It is free from matrix effects. Yet it works for full range of concentrations.

The Basic Decoding Equation (6) contains two unknowns (X_i & k_i) and three measured data (X_s, I_i & I_s). Given composition X_i in synthetic mixture, the constant k_i can be calculated. Given the constant k_i in an unknown mixture, the composition X_i can be calculated. In other words, a single XRD or XRF scan quantifies the chemical compounds or elements in any complex mixtures. Because k_i is a characteristic constant of each chemical compound or chemical element, it needs to be measured only once for all.

The reference standard (X_s) plays multiple roles: 1. It puts all X-ray intensity data on the same scale. 2. It acts as a probe or spy and flashes back its findings in X-ray signals. 3. It defines the characteristic constant slope of calibration line. 4. It functions as an internal standard.

The physics of XRD and XRF are fundamentally different. However, both techniques share the same primary X-rays. Both diffraction and emission take place simultaneously. The X-ray instrument selectively collects the coded signals either by Bragg angle (XRD) or by wavelength (XRF). The primary X-rays, the diffracted X-rays, and the emitted X-rays should obey the same Adiabatic Principle of X-rays (Chung, 1974b).

3. Application of the decoding formula

3.1 XRD: All components are crystalline: No reference standard is required. We have n unknowns (X_i), which must satisfy the following (n + 1) equations. These (n+1) equations can be conveniently treated in terms of matrix algebra:

$$I_i = k_i \bullet X_i, \quad i = 1 \text{ to } n \qquad \text{and} \qquad \sum_1^n \mathrm{Xi} = 1$$

$$\begin{vmatrix} k_1 & 0 & 0 & \ldots & 0 \\ 0 & k_2 & 0 & \ldots & 0 \\ 0 & 0 & k_3 & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots \end{vmatrix} \bullet \begin{vmatrix} X_1 \\ X_2 \\ X_3 \\ : \end{vmatrix} = \begin{vmatrix} I_1 \\ I_2 \\ I_3 \\ : \end{vmatrix}$$

$$\begin{array}{l} | \;\; 0 \quad 0 \quad 0 \quad \ldots\ldots \quad k_n \;\; | \qquad | \; X_n \; | \qquad\qquad | \;\; I_n \;\; | \\ | \;\; 1 \quad 1 \quad 1 \quad \ldots\ldots \quad 1 \;\; | \qquad\qquad\qquad\qquad\;\; | \;\; 1 \;\; | \end{array}$$

When the matrix equation, **KX = I,** has a solution, the solution is unique if and only if the rank of the **(K)** matrix is equal to the rank of the (**K, I**) matrix, which is also equal to the number of unknowns. The unique solution has the following symmetrical form:

$$X_i = \left[\frac{k_i}{I_i} \sum_1^n \frac{I_i}{k_i} \right]^{-1} \qquad \text{It implies the Law of Binary Mixtures} \qquad (7)$$

Equation (7) involves only intensity (I_i) data. The k_i's are characteristic constants. The weight fractions (X_i) of all components can be determined with one single XRD scan of the original mixture. It establishes the Law of Binary Mixtures (See next sections), which leads to the simplest way to decode complex mixtures as demonstrated by the three sets of experimental data.

3.2 XRD: Some components are amorphous: A reference standard is required for this case. Apply equation (6) to each identified component. We have

$$X_o = X_1 + X_2 + \cdots + X_n = \frac{X_s}{I_s}\left(\frac{I_1}{k_1} + \frac{I_2}{k_2} + \cdots + \frac{I_n}{k_n}\right) = \frac{X_s}{I_s} \sum_1^n \frac{I_i}{k_i}$$

Rearrange we get $$\sum_1^n \frac{I_i}{k_i} \; \overset{<}{\underset{>}{=}} \; \frac{X_o}{X_s} \bullet I_s \qquad \text{The discriminant equation for XRD} \qquad (8)$$

Where X_o = weight fraction (% wt) of original mixture.
< indicates presence of amorphous contents.
= indicates all components are crystalline.
> indicates wrong experimental data.

Equation (8) determines if amorphous contents are present and how much in the original sample.

3.3 XRF: Regardless Crystalline or amorphous

No matter the mixture is crystalline or amorphous. X-ray Fluorescence can assess all elements heavier than oxygen. A reference standard is always required for XRF. Apply Equation (6) to each element sought. Equation (7) may even work for metallic alloys (pending further research work). Equation (8) applies to XRD only.

Equations (6) (7) & (8) are the essence of the proposed Unified and Simplified Theory of XRD & XRF. Equation (6) is the basic decoding formula, applies to both XRD & XRF for any mixtures. It is the key to solve most problems in XRD & XRF. Equation (7) transforms any complex mixtures into a set of binary mixtures for both XRD & XRF (see section on Law of Binary Mixtures). Equation (8) works for XRD only. It determines if amorphous contents are present and how much.

For both XRD & XRF, only X-ray intensities (I_i & I_s) are to be measured from a single sample preparation. Other factors are either constants (k_i & k_s) or known quantities (X_s & X_o). Consequently, one single X-ray scan of one sample preparation quantifies all components with one decoding formula. Be sure the prepared sample is a homogeneous mixture. Certainly, the average intensity of repeated scans improves the precision.

4. Specific intensity of XRD & XRF

For easy comparison of the same property of different materials, usually a pure compound is assigned as reference standard. For example, the specific gravity of gold is 19.3, which means that the mass of gold is 19.3 times as heavy as the mass of water at 4˚C. The ubiquitous water is assigned as reference standard. Note that both the density and specific gravity of water are defined to be exactly one (1.00). The word "specific" means per unit mass, such as the specific impulse of rocket fuel in space ship. In order to put all X-ray intensity data on the same scale, let us define a new term Specific Intensity (k_i) of any chemical element or chemical compound (i) as follows:

$$\text{Specific Intensity} = \frac{\text{XRD or XRF intensity of 1.00\% of component } (I_i)}{\text{XRD or XRF intensity of 1.00\% of reference standard } (I_s)} = \left(\frac{I_i}{I_s}\right)_{1\%\ \text{each}} \qquad (9)$$

Rearrange the basic decoding equation (6), we have:

$$k_i = \frac{I_i / X_i}{I_s / X_s} = \left(\frac{I_i}{I_s}\right)_{1\%\ \text{each}} = \left(\frac{I_i}{I_s}\right)_{50/50} = \text{Specific Intensity} \qquad (10)$$

$$= \text{slope of Equation (5) \& (6) for both XRD \& XRF}$$

A set of Specific Intensity (k_i) can be determined from a synthetic mixture for either compounds (XRD) or elements (XRF).

The Specific Intensity (k_i) indicates how strong is the diffracted or emitted X-rays relative to that of the reference standard (Y_2O_3 or αAl_2O_3 for XRD, Y in Y_2O_3 for XRF). We have $k_s = 1.00$ by definition. Yttrium Y is a rare element, most likely it is not present in the original sample. High purity chemical grade Y_2O_3 powder is white, stable, inexpensive, and readily available.

Equations (9) & (10) display five roles of the specific intensity (k_i): 1. It puts all X-ray intensity data on the same scale. 2. It is the slope of the basic decoding formula. 3. It is a characteristic constant of each chemical element or compound. 4. It allows simultaneous determination of a set of k_i with one sample preparation. 5. It unifies and simplifies quantitative XRD & XRF analyses.

Three new discoveries led to the 1. Eliminate the matrix effects; 2. Discard the calibration lines; and 3. Establish the Law of Binary Mixtures. Consequently, a single X-ray scan of one sample preparation quantifies all components sought in any mixture. It reduces over 80% lab work required by current practice. Three sets of experimental data are presented to illustrate lab practice. Its precision has been evaluated statistically to be ± 5% or better, which is sufficient to solve most problems.

5. The law of binary mixtures

The decoding formula Equation (6), leads to the unique solution Equation (7). Equation (7) establishes the Law of Binary Mixture: The plot of intensity ratio to the weight ratio of any two components is a straight line passing through the origin with a slope equal to the ratio of corresponding specific intensities. This intensity-concentration relationship between each and every pair of components in a multi-component system is not disturbed by the presence or absence of other components. In other words, each pair of components in a multi-component mixture forms an isolated (adiabatic) unit, immune (adiabatic) from the coexistence of other components.

Implant known amount of a reference standard (Y_2O_3 or αAl_2O_3) into any complex mixture and couple it with each component sought. The complex mixture becomes a set of binary mixtures, the simplest mixture. Moreover, one of the two components in each binary mixture is the known reference standard. It makes each binary mixture “simpler than the simplest mixture”, a strange but hard fact. It empowers the Unified Theory of XRD & XRF as the simplest way to quantify any mixtures. The term Law of Binary Mixture is more intuitive than the esoteric term Adiabatic Principle (Chung, 1974b).

Equation (6) and (7) eliminates the matrix effects, the calibration lines, and the certified standards. Just one single XRD or XRF scan gives the weight fractions of all components sought. Moreover, the weight fraction is expressed in terms of ratios, I_i / I_j and k_i / k_j ($i, j = 1, 2, \cdots, n$). Therefore, many disturbing factors are mutually cancelled, including matrix factors, specimen thickness, specimen density, residual stress, micro-absorption, preferred orientation, crystallinity, extinction, particle size and size distribution, specimen position, instrumental drifting, and others.

6. Numerical Example for Quantitative XRD analyses

The key point of the unified theory is to measure the Specific Intensities (k_i) of components in a synthetic mixture by Equation (6), then determine the weight fractions of components sought (X_i) in unknown mixtures by Equations (6) (7) or (8). Note that Equations (7) & (8) are derived from the basic Equation (6).

Three numerical examples are presented to illustrate the applications of the three working equations (6), (7) & (8).The compositions and X-ray data are summarized in the corresponding Tables. The strongest resolved X-ray peak was chosen for intensity measurements. In order to avoid repetitions, the detailed lab procedures are referred to the cited references. The numerical calculations are detailed for easy references.

6.1 All components are crystalline.

Because the Specific Intensity, (k_i) is the characteristic constant of each component i, the XRD intensities (I_i) from a single scan of one sample preparation are the only experimental data required to calculate X_i, The set of data in Table 1 illustrates the applications of the working Equations (6), (7) & (8):

Table 1. All components are crystalline.

	Weight, g	% Weight X_i Known	Found	XRD, cps I_i	Specific Intensity k_i, Constant slope
ZnO	0.5554	32.54	32.5	4036	4.27
CdO	0.2266	13.27	13.3	3029	7.85
LiF	0.3712	21.74	21.8	778	1.23
αAl_2O_3	0.5539	32.45	---	943	1.00

• **Basic Decoding Equation (6):** Let the ZnO, CdO & LiF in Table 1 are the components (X_i) in the original mixture. The αAl_2O_3 is added as the Reference Standard (X_s). Apply the Basic Decoding Equation (6): Giving I_i & k_i, we can calculate X_i. Given I_i & X_i we can calculate k_i. We have:

Given I_i & k_i, calculate X_i **Given I_i & X_i, calculate k_i**

$$X_{ZnO} = \frac{32.45}{\quad} \cdot \frac{4036}{\quad} = 32.5 \quad \text{or} \quad k_{ZnO} = \frac{32.45}{\quad} \cdot \frac{4036}{\quad} = 4.27$$

$$4.27 \quad 943 \qquad\qquad 32.54 \quad 943$$

$$X_{CdO} = \frac{32.45}{7.85} \bullet \frac{3029}{943} = 13.3 \quad \text{or} \quad k_{CdO} = \frac{32.45}{13.28} \bullet \frac{3029}{943} = 7.85$$

$$X_{LiF} = \frac{32.45}{1.23} \bullet \frac{778}{943} = 21.8 \quad \text{or} \quad k_{LiF} = \frac{32.45}{21.74} \bullet \frac{778}{943} = 1.23$$

$$X_{Al2O3} = \frac{32.45}{1.00} \bullet \frac{943}{943} = 32.5 \quad \text{or} \quad k_{Al2O3} = \frac{32.45}{32.45} \bullet \frac{943}{943} = 1.00$$

• **Adiabatic Equation (7):** Let all four chemicals in Table 1 are components of the original mixture. No Reference standard is required. One single XRD scan of the original mixture quantifies its composition. Apply the Adiabatic Equation (7). We have:

$$X_{ZnO} = [\, 1 + \frac{4.27}{4036} (\frac{3029}{7.85} + \frac{778}{1.23} + \frac{943}{1.00})]^{-1} = 32.5$$

$$X_{CdO} = [\, 1 + \frac{7.85}{3029} (\frac{4036}{4.27} + \frac{778}{1.23} + \frac{943}{1.00})]^{-1} = 13.3$$

$$X_{LiF} = [\, 1 + \frac{1.23}{778} (\frac{3029}{7.85} + \frac{4036}{4.27} + \frac{943}{1.00})]^{-1} = 21.8$$

$$X_{Al2O3} = [\, 1 + \frac{1.00}{943} (\frac{4036}{4.27} + \frac{3029}{7.85} + \frac{778}{1.23})]^{-1} = 32.5$$

• **Discriminant Equation (8):** Reference standard is required. Apply Equation (8) to check if amorphous content present and how much. Referring to the calculated data from Equation (6), we have:

$$\sum_1^n \frac{I_i}{k_i} \overset{<}{\underset{>}{=}} \frac{X_o}{X_s} \bullet I_s \tag{8}$$

Where $X_0 = 67.5$ % and $X_s = X_{Al2O3} = 32.5$ %.

Left side of Equation (8): $$\sum_1^n \frac{I_i}{k_i} = \frac{4036}{4.27} + \frac{3029}{7.85} + \frac{778}{1.23} = 1963$$

Right side of Equation (8): $$\frac{X_o}{X_s} \bullet I_s = \frac{67.5}{32.5} \bullet 943 = 1959$$

The left side is almost equal to the right side, 1959 ~ 1963, which indicates no amorphous content.

6.2 Some components are amorphous.

A reference standard αAl_2O_3 is required in this case. Equation (6) gives the weight fractions of all identified crystalline components. Equation (8) determines whether amorphous materials are present and how much. Note that k_{ZnO} = 4.35, k_{CaCO3} = 2.98 in Table 2 are averages from prior work. A good estimate of amorphous content (Silica gel) is obtained as shown in Table 2.

Table 2. Some components are amorphous and/or unidentified

Component	Composition gram	Intensity I_i (cps)	Sp. Int. k_i	% wt. in admix. Known	% wt. in admix. Found	% wt in orig. mix. Known	% wt in orig. mix. Found
ZnO	0.9037	4661	4.35	34.43	36.4	43.8	46.3
$CaCO_3$	0.7351	2298	2.98	28.00	26.2	35.6	33.4
Silica gel	0.4234	0	–	16.13	(16.0)	20.5	(20.4)
Added Ref. Std.							
αAl_2O_3	0.5629	631	1.00	21.44	----	0	0

Total weight of original mixture = 2.0622 grams (no αAl_2O_3).
Total weight of admixture = 2.6251 grams (with αAl_2O_3).

According to basic decoding Equation (6):

$$X_{ZnO} = \frac{21.44}{4.35} \bullet \frac{4661}{631} = 36.4\ \%$$

$$X_{CaCO3} = \frac{21.44}{2.98} \bullet \frac{2298}{631} = 26.2\ \%$$

Amorphous content = 100 – 36.4 – 26.2 – 21.4 = 16.0 % in admixture (with αAl_2O_3) or

Apply Equation (8) we have: $X_o = 78.56\ \%$, $X_s = 21.44\ \%$

$$\sum_1^n \frac{I_i}{k_i} = \frac{4661}{4.35} + \frac{2298}{2.98} = 1842, \quad \text{and} \quad \frac{X_o}{X_s} \bullet I_s = \frac{78.56 \times 631}{21.44} = 2312$$

The left side is much smaller than the right side of Equation (8), 1842 << 2312. It indicates the presence of amorphous contents, which can be determined by mass balance. Note that all the symbols in Equations (6) & (8) are referring to the admixture (original sample plus reference standard). Equation (7) has no reference standard. Equation (11) converts X_i to X_i^o, the weight fraction of component (i) in original sample.

$$X_i^o = \frac{X_i}{1 - X_s} = X_i \bullet \frac{\text{Wt. of admixture}}{\text{Wt. of original mixture}} \qquad (11)$$

$$X_{ZnO}^o = 36.4 \bullet \frac{2.6251}{2.0622} = 46.3\ \%$$

$$X_{CaCO3}^o = 26.2 \bullet \frac{2.6251}{2.0622} = 33.4\ \%$$

$$X_{\text{Silica gel}}^o = 16.0 \bullet \frac{2.6251}{2.0622} = 20.3\ \% = \text{Amorphous content in original mixture.}$$

Double check for admixture: 36.41 + 26.20 + 16.00 + 21.44 = 100% (with Al_2O_3).
Double check for original sample: 46.3 + 33.4 + 20.3 = 100% (without Al_2O_3).

7. Numerical Example for Quantitative XRF analysis

A reference standard (Y_2O_3) is required in this case. It shows the application of Equations (6) for XRF, no matter crystalline or amorphous.

Add known amount of reference standard (Y_2O_3) into the synthetic sample. Grind and homogenize the admixture. Run XRF experiments. All XRF intensity data are from one single scan of one sample preparation. Average intensity from duplicate scans is used to improve precision. Just like the XRD analysis, given the measured intensity (I_i) and the constant specific intensity (k_i), the composition (X_i & X_i^0) can be calculated by Equations (6) & (11).

Table 3 lists the measured intensities (I_i) and the average specific intensities (k_i) of prior work. All other data are results of calculations. The experimentally “found % weights” from XRF agree well with the “known % weights” of the synthetic mixture.

The X-ray intensities (I_i) in Table 3 are the only experimental data required to quantify all components sought. The k_i’s are the average Specific Intensities (characteristic constant slopes of calibration lines) from prior work. All other data in Table 3 are results of calculations. Equation (6) gives X_i. Equation (11) converts X_i (% weight in admixture) to X_i° (% weight in original synthetic sample).

Note that given the composition (X_i) and intensity (I_i) data of the synthetic mixture, a set of specific intensities (k_i) can be determined. All k_i ‘s are characteristic constants, which vary within experimental errors.

Table 3. Access all elements heavier than oxygen in mixture.

Composition, g		I_i, cps XRF Intensity	k_i, Spec. Intensity Constant slope from prior work	X_i, Weight % in Admixture		X^0_i, Weight % in Original Mix.	
				Known	Found	Known	Found
$BaSO_4$	0.0695						
Ba		124	1.96	2.60	2.55	2.83	2.78
S		0.97	0.0635	0.61	0.61	0.66	0.66
ZnO	0.3677						
Zn		1357	2.88	18.8	19.0	20.5	20.7
K_2HPO_4	1.0071						
K		464	0.646	28.8	28.9	31.3	31.5
P		11.3	0.0393	11.4	11.6	12.4	12.6
Reference Standard							
Y_2O_3	0.1277						
Y		159	1.00	6.40	---	0	0

Total weight of original sample (without Y_2O_3) = 1.4443 g. that of admixture (with Y_2O_3) = 1.5720 g.

$$X_{Ba} = \frac{6.40}{1.96} \bullet \frac{124}{159} = 2.55\ \% \qquad X_{Ba}° = 2.55 \bullet \frac{1.5720}{1.4443} = 2.78\ \%$$

$$X_{Zn} = \frac{6.40}{2.88} \bullet \frac{1357}{159} = 19.0\ \% \qquad X_{Zn}° = 19.0 \bullet \frac{1.5720}{1.4443} = 20.7\ \%,$$

$$X_{K} = \frac{6.40}{0.646} \bullet \frac{464}{159} = 28.9\ \% \qquad X_{K}° = 28.9 \bullet \frac{1.5720}{1.4443} = 31.5\ \%,$$

$$X_{S} = \frac{6.40}{0.0635} \bullet \frac{0.97}{159} = = 0.61\ \% \qquad X_{S}° = 0.61 \bullet \frac{1.5720}{1.4443} = 0.66\ \%,$$

$$X_{P} = \frac{6.40}{0.0393} \bullet \frac{11.3}{159} = 11.6\ \%. \qquad X_{P}° = 11.6 \bullet \frac{1.5720}{1.4443} = 12.6\ \%,$$

$$X_{Y} = \frac{6.4}{1.00} \bullet \frac{159}{159} = 6.40\ \% \qquad X_{Y}° = 0.00\ (I_{Y} = 0.00,\ \text{No Yttrium})$$

If the XRF job were done by the book (Muller, 1972; Herglotz & Birks, 1978; Jenkins et al., 2002; Grieken & Markowicz, 2002), it would require 5 calibration lines for the 5 elements sought. Each calibration line needs 3 data points plus the sample itself. That means 5x4=20 times more sample preparations from certified standards, 20 times more X-ray scans, 20 times more intensity measurements, 20 times more calculations, and 20 times more plotting. This situation is much the same for the XRD analyses.

In summary, the Unified and Simplified Theory of Quantitative XRD & XRF has been practiced in our lab. It reduces by over 80% of the lab work required by current practice. Statistical evaluation (Chung, 1974a,b, 1975c, 2016; Chung & Smith, 2000) gives a precision of ± 5% or better, which is sufficient to solve most industrial problems. Note that the Rietveld refinement whole pattern fitting methods have the potential to approach the precision limit of ± 1% at the expense of much more time for data collection and processing (Chung & Smith, 2000; Hubbard et al. 1983; Snyder, 1992; Smith et al., 1987; Bish & Howard, 1988).

7. Conclusions

New insights establish three laws of quantitative XRD & XRF analysis. The first two laws change the current concept of quantitative XRD & XRF analyses. The third law unifies and simplifies the quantitative XRD & XRF analyses.

1. The law of zero matrix effects: Every component in the same specimen has identical matrix factors (µ, ϱ & d), which can be exactly cancelled mathematically. There is no matrix problem from the very beginning.

2. The law of constant slope: The slope of calibration line for any chemical compound (XRD) or chemical element (XRF) is a characteristic constant (i.e. Specific Intensity, k_i). A set of Specific Intensities can be easily determined, thus eliminates all calibration work.

3. The law of binary mixtures: It transforms any complex mixture into a set of the simplest binary mixtures. That means each binary mixture has a component of known % weight. The % weight of the other component is obvious.

These three laws of XRD & XRF realize six advantages: 1. eliminate the matrix effects, 2. evade the calibration lines, 3. one decoding formula applies to both XRD & XRF, 4. It works for full range of concentrations, 5. one single X-ray scan of one sample preparation decodes all % weights, and 6. Reduce lab work by some 80% required by current practice. It amounts to a breakthrough in quantitative XRD & XRF analysis.

9. References

Azaroff, L. V. (**1968**). *Elements of X-ray Crystallography*, p. 202. New York: McGraw Hill.

Bish, D. L. & Howard S. A. (**1988**). "Quantitative Phase Analysis Using the Rietveld Method." *J. Appl. Cryst*. 21, 86-91.

Bunn, C. W. (**1961**). *Chemical Crystallography*, 2nd ed. p. 223. London: Oxford University Press.

Chung, F. H. (**1974a**). "Quantitative Interpretation of X-Ray Diffraction Patterns of Mixtures. I. Matrix Flushing Theory for Multi-Component Analysis." *J. Appl. Cryst*. **7**: 519-525.

Chung, F. H. (**1974b**). "Quantitative Interpretation of X-Ray Diffraction Patterns of Mixtures. II. Adiabatic Principle of X-Ray Diffraction Analysis." *J. Appl. Cryst*. **7**: 526-531.

Chung, F. H. (**1974c**). “A New X-Ray Diffraction Method for Quantitative Multi-component Analyses.” Advances in X-Ray Analysis, Vol. **17**, pp. 106-115.

Chung, F. H. (**1975**). “Quantitative Interpretation of X-Ray Diffraction Patterns of Mixtures. III. Simultaneous Determination of a Set of Reference Intensities.” *J. Appl. Cryst*. **8**: 17-19.

Chung, F. H. (**2017**). “Unified Theory for Decoding the Signals from X-Ray Fluorescence and X-Ray Diffraction of Mixtures.” Applied Spectroscopy, Vol. **71**(5), pp. 1060-1068.

Chung, F. H. (**2018**). “Quantitative XRD & XRF Analyses of Mixtures — Unified and Simplified”. J. Appl. Cryst. **51**: 789-795.

Chung, F. H., Lentz, A. J. & Scott, R. W. (**1974**). “A Versatile Thin-Film Method for Quantitative X-Ray Emission Analysis.” X-Ray Spectroscopy. **3**: 172-175.

Chung, F. H. & Smith D. K. (**2000**). *Industrial Applications of X-Ray Diffraction*. pp. 3, 13, 37 & 511. New York: Marcel Dekker.

Clark, G. L. & Reynolds D. H. (**1936a**). At University of Illinois, adapted the highly developed quantitative “Internal Standard” method of ultraviolet spectroscopy for quantitative XRD analysis.

Clark, G. L. & Reynolds D. H. (**1936b**). “Quantitative Analysis of Mine Dusts.” Ind. Eng. Chem., Anal. Ed. **8**. p. 36.

Cohen, L. H. & Smith D. K. (**1989**). “Thin-Specimen X-ray Fluorescence Analysis of Major Elements in Silicate Rocks.” Anal. Chem. **61**: 1837-1840.

Copeland, L. E. & Bragg, R. H. (**1958**). “Quantitative X-Ray Diffraction Analysis.” Anal. Chem. **30**(2), 196-201.

Cullity, B. D. & Stock, S. R. (**2001**). *Elements of X-Ray Diffraction*, 3rd Edition. New Jersey: Prentice Hall.

Grieken, R. V. & Markowicz A. A. (**2002**). *Handbook of X-ray Spectrometry*: Methods and Techniques, 2nd ed. New York: Marcel Dekker.

Herglotz, H. K. & Birks, L. S. (**1978**). *X-Ray Spectrometry*. New York: Marcel Dekker.

Hubbard, C. R. Robbins, C. R.& Snyder R. L. (**1983**). “XRD Quantitative Analysis Using the NBS Quant82 System.” Adv. X-Ray Anal. **26**:149-157.

Jenkins, R., Gould R. W. & Gedcke D. (**2002**). *Quantitative X-Ray Spectrometry*, 2nd ed. New York: Marcel Dekker.

Jenkins, R. & Snyder R. L. (**1995**). *Introduction to X-ray Powder Diffractometry*. New York: John Wiley and Sons. pp. 369 - 376.

Klug, H. P. & Alexander L. E. (**1974**). *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. New York: John Wiley & Sons.

MIT X-ray SEF List of Resources (**2018**). Textbooks on X-Ray Diffraction. Website: http://prism.mit.edu/xray/oldsite/resources.htm.

Muller, R. O. (**1972**). *Spectrochemical Analysis by X-Ray Fluorescence*. pp. 59-61. New York: Plenum Press.

Rietveld, H. M. (**1969**). J. Appl. Cryst.**2**, 65-71.

Scheibe G. (**1933**). *Chemissche Spektralanalyse*, Physikalische Methoden der Analytischen Chemie, Vol. **1**, p.108 and pp. 125-130. Leipzig, Akademische Verlagsgesellschaft (in German).

Smith, D. K., Johnson G. G., Scheible, A., Wims, A. M., Johnson, J. L. & Ullmann, G (**1987**). “Quantitative X-ray Powder Diffraction Method Using the Full Diffraction Pattern.” Powder Diffraction, **2** (2): pp.73-77.

Snyder, R. L. (**1992**). “The Use of Reference Ratios in X-ray Quantitative Analysis.” Powder Diffraction. **7**: pp. 186-193.