Experimental Study and Matrix Effect Correction of Pseudo-binary Samples in XRF Analysis

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Abstract. This basic study conducted an X-ray fluorescence (XRF) analysis on pseudo-binary samples, which emphasis on the binary influence coefficient and correction for matrix effects. The Ti-V, V-Ti, Ti-Fe, Fe-Ti, V-Fe and Fe-V samples were confected and measured by XRF analysis using a Si-PIN detector. These coefficients were calculated using mathematical models proposed through the Lachance-Traill algorithm, which can be applied in practice via an efficient calibration procedure. For the content measurement, the maximum absolute error decreased from 5.92% to 0.27%, and the relative error decreased from 14.84% to 0.66% via fitting correction for matrix effects. This study describes and emphasizes the application of the binary influence coefficient and fitting correction method.

1. Introduction
X-ray fluorescence (XRF) analysis technology has been widely applied due to its advantage of non-destructive and fast analysis, and easy application. For instance, energy dispersive fluorescence analysis equipment has been widely used in chemical, geological, environmental and other fields due to its portability. XRF has been utilized to analyse unknown samples for several decades. Under excitement through X-ray sources, the characteristics of the X-ray fluorescence elements measured were emitted through the energy level transition in the inner-shell electron. By measuring the energy and intensity characteristics of X-ray fluorescence, the element type and concentration for unknown samples could be determined. However, differences exist between the standard sample and unknown sample, such as physical structure, chemical composition and so on. Therefore, there would be some deviations in the quantitative results. This is called the matrix effect. The variety of chemical composition and physical property in these samples would affect these analytical results, which presented as an enhancement or absorption. Due to the complex ingredients in these samples, the matrix effects would bring in an unacceptable error in XRF measurements. With the proposal of the Sherman Equation, many scholars have conducted a number of working XRF analyses [1-4]. Ying Xiaohu corrected the matrix effects of Cr-Fe-Ni by directly using theoretical alpha coefficients in stainless steel measurements [5]. This method can achieve good results in analyzing the element content, which varies greatly in unknown samples. Furthermore, this method may also appropriately extend the calibration curve. Li Siwei corrected the matrix effects of lead-copper alloy samples through the r-α coefficient [6]. This method reduced the number of required standards, and their analysis results are better than those through the fundamental parameter method or theoretical alpha coefficients method. Li Zhe measured the element Ti and Fe in ore samples by EDXRF [7], and corrected the non-linear relationships between the characteristics X-ray fluorescence counts and its content by neural network technology. Compared with chemical analysis methods, 65.4% of the...
sample’s relative error was less than 1%, and the rest were less than 3%. This result could meet the requirements for the industrial production equipment analysis, which requires a relative error of less than 5%. Most of these methods limit the specific range, as well as the range of applications [8-11]. This study attempted to conduct matrix effects analysis in EDXRF by establishing pseudo-binary samples and designing experiments to obtain two-dimensional coefficients. In addition, it also discusses the binary influence coefficient and correction for matrix effects in pseudo-binary samples, such as samples of Ti-V, V-Ti, Ti-Fe, Fe-Ti, V-Fe and Fe-V. The Lachance-Traill algorithm and fitting correction method were applied.

2. Binary influence coefficient

In these pseudo-binary samples, the elements comprise of j and i. These samples can be expressed as the composition \((C_i, C_j)\), and

\[ C_i + C_j = 100\% \]

With monochromatic excitation sources, \(\beta_{ij}\) is the absorption factor, and \(\delta_{ij}\) is the enhancement factor. According to the Sherman Equation [12],

\[
\beta_{ij} = \frac{\mu_i(\lambda_k) + \mu_j(\lambda_k)}{\mu_i(\lambda_k) + \mu_j(\lambda_k)} - 1
\]

\[ \delta_{ij} = \frac{1}{2} D_j(\lambda_k) D_i(\lambda_k) k_j \mu_j(\lambda_k) \frac{\mu_i(\lambda_k)}{\mu_i(\lambda_k)} P_0(\lambda_k) \]

The parameter, \(P_0(\lambda_k)\), presented in these two previous equations was defined by

\[
P_0(\lambda_k) = \frac{1}{\mu_i(\lambda_k)} \ln[1 + \frac{\mu_j(\lambda_k)}{\mu_i(\lambda_k)}] + \frac{1}{\mu_j(\lambda_k)} \ln[1 + \frac{\mu_i(\lambda_k)}{\mu_j(\lambda_k)}]
\]

In Equations (2) to (4), the meaning of each parameter is as follows:

- \(\mu_i(\lambda_k)\) The mass absorption coefficient of the i element on X-ray, in which the wavelength is \(\lambda_k\);
- \(D_j(\lambda_k)\) 1 if the incident radiation \(\lambda_k \leq \lambda_{abs\, edge}\) of the j element,
- 0 in all other cases;
- \(D_i(\lambda_k)\) 1 if the fluorescence radiation \(\lambda_j \leq \lambda_{abs\, edge}\) of the i element,
- 0 in all other cases;
- \(k_j\) The absorption mutation factor;
- \(\mu_{i,}, \mu_{i,}', \mu_{i,}''\) The mass absorption coefficient, \(\text{cm}^2\cdot\text{g}^{-1}\)

and

\[
\mu_i(\lambda_k) = \sum_{n=1}^{N} \mu_n(\lambda_k) C_n \csc \phi
\]

\[
\mu_j(\lambda_k) = \sum_{n=1}^{N} \mu_n(\lambda_k) C_n \csc \phi
\]

Where \(N\) is the amount of elements in the sample, \(\phi\) is the incidence angle and \(\phi\) is the exit angle.

In addition, with polychromatic excitation sources, \(\alpha_{ij}\) is the absorption factor, and \(\varepsilon_{ij}\) is the enhancement factor. According to the Rousseau Equation [13],

\[
\alpha_{ij} = \frac{\sum W(\lambda_k) \beta_{ij}(\lambda_k)}{\sum W(\lambda_k)} \quad \text{(7)}
\]

\[
\varepsilon_{ij} = \frac{\sum W(\lambda_k) \delta_{ij}(\lambda_k)}{\sum W(\lambda_k)} \quad \text{(8)}
\]

The weighting factor, \(W(\lambda_k)\), presented in the two previous equations was defined by
In Equation (9), $\mu^*$ is the effective mass absorption coefficient, which is defined by

$$
\mu^* = \mu_i(\lambda_j) + \mu_j(\lambda_i)
$$

According to Equation (1) and the Lachance-Traill algorithm [14-15], the binary influence coefficient $A_{ij}$ can be calculated by

$$
A_{ij} = \frac{\alpha_i - \epsilon_i}{1 + \epsilon_i(1-C_i)} = \frac{\alpha_i - \epsilon_i}{1 + \epsilon_iC_j}
$$

Actually, the measurement results were determined through numerous factors, such as absorption effect, enhancement effect, and so on. This study used the binary influence coefficient $A_{ij}$, which is a comparative statistic, in order to discuss the matrix effects in pseudo-binary samples.

### 3. Sample preparation

This study configured a series of samples using a chemical analytical reagent, such as Fe$_2$O$_3$ powder (the content of Fe was 70%), TiO$_2$ powder (the content of Ti was 60%), and V$_2$O$_5$ powder (the content of V was 56%). For the sample’s composition ($C_i$, $C_j$) in the pseudo-binary system, the $i$ element is the primary base, and the $j$ element is the so-called impurity. The content of these pseudo-binary samples is presented in Table 1.

| Table 1. Content of the pseudo-binary samples |
|-----------------------------------------------|
| Fe-V Samples | V-Fe Samples | V-Ti Samples | Ti-V Samples | Fe-Ti Samples | Ti-Fe Samples |
| $C_F$ | $C_V$ | $C_F$ | $C_V$ | $C_F$ | $C_V$ | $C_F$ | $C_V$ | $C_F$ | $C_V$ | $C_F$ | $C_V$ |
| 0.05 | 0.52 | 0.05 | 0.66 | 0.05 | 0.63 | 0.05 | 0.52 | 0.05 | 0.56 | 0.05 | 0.66 |
| 0.10 | 0.49 | 0.10 | 0.60 | 0.10 | 0.59 | 0.10 | 0.48 | 0.10 | 0.52 | 0.10 | 0.61 |
| 0.15 | 0.44 | 0.15 | 0.52 | 0.15 | 0.52 | 0.15 | 0.42 | 0.15 | 0.48 | 0.15 | 0.58 |
| 0.20 | 0.39 | 0.20 | 0.45 | 0.20 | 0.45 | 0.20 | 0.38 | 0.20 | 0.43 | 0.20 | 0.50 |
| 0.25 | 0.36 | 0.25 | 0.41 | 0.25 | 0.40 | 0.25 | 0.32 | 0.25 | 0.39 | 0.25 | 0.42 |
| 0.30 | 0.33 | 0.30 | 0.34 | 0.30 | 0.32 | 0.30 | 0.28 | 0.30 | 0.35 | 0.30 | 0.35 |
| 0.35 | 0.29 | 0.35 | 0.26 | 0.35 | 0.27 | 0.35 | 0.25 | 0.35 | 0.30 | 0.35 | 0.34 |
| 0.40 | 0.24 | 0.40 | 0.21 | 0.40 | 0.20 | 0.40 | 0.20 | 0.40 | 0.26 | 0.40 | 0.24 |
| 0.45 | 0.21 | 0.45 | 0.16 | 0.45 | 0.16 | 0.45 | 0.16 | 0.45 | 0.22 | 0.45 | 0.17 |
| 0.50 | 0.16 | 0.50 | 0.08 | 0.50 | 0.09 | 0.50 | 0.09 | 0.50 | 0.18 | 0.50 | 0.14 |
| 0.55 | 0.12 | 0.55 | 0.03 | 0.55 | 0.02 | 0.55 | 0.03 | 0.55 | 0.15 | 0.55 | 0.10 |
| 0.60 | 0.09 | 0.56 | 0.00 | 0.56 | 0.00 | 0.60 | 0.00 | 0.60 | 0.10 | 0.60 | 0.06 |
| 0.65 | 0.04 | - | - | - | - | - | - | 0.65 | 0.04 | 0.65 | 0.03 |
| 0.70 | 0.00 | - | - | - | - | - | - | 0.70 | 0.00 | 0.70 | 0.00 |

Each sample was made into sheets using the pressing method. The best pressure was 25 KN. Recovery time was 90 seconds. Every sample was placed in a dryer for one hour at a temperature of 105-110°C. This sample preparation can reduce its impact on measurement results, such as the uniformity effect, particle distribution effect, moisture effect, and so on.

The detector of the X-ray fluorescence analyzer was the Si-PIN detector, which was produced by AMPTEK INC. Its main technical indicators were as follows: the energy resolution was 150-180 eV ($^{55}$Fe, 8.90 KeV), the scope of analysis was 0.001%-99.999%, the measuring range was 2-20 KeV, measuring time was <200 seconds, repeatability was <5%, stability was <0.05%, and power consumption was 300 W.
4. Sample preparation
The mass absorption coefficient \( \mu \) is the sum of the optical absorption coefficient, coherent mass absorption coefficient, and incoherent mass absorption coefficient. The primary X-ray intensity \( E_g \) was 12.5 \( keV \), and the content of the sample \((C, C)\) was 100%. The X-ray characteristic energy, wavelength and mass absorption coefficient are presented in Table 2 [16].

**Table 2.** Mass attenuation coefficients of Ti, V and Fe elements

| X-ray’s Energy and Wavelength (\(keV, Å\)) | Mass attenuation coefficient(\(cm^2·g^{-1}\)) |
|-------------------------------------------|-----------------------------------------------|
| \(Ti_kβ(4.510, 2.749)\)                  | 120.00                                        |
| \(V_kβ(4.952, 2.503)\)                   | 89.00                                         |
| \(Fe_kβ(6.403, 1.936)\)                  | 386.00                                        |

Absorption mutation factor \( k_T = 0.8842, k_V = 0.8828, k_{Fe} = 0.8786\) [17].

The calculation and measurement results are shown in Figures 1-3. These figures represent the visual analysis of the relationship between \(C_i\) and \(A_{ij}\). When \(A_{ij}\) was positive, the element was absorbed and the \(j\) element was enhanced in the sample \((C_i, C_j)\). However, the consequences reversed when \(A_{ij}\) was negative.

For Fe-V samples (Fig. 1), the binary influence coefficients are quite negative. \(A_{Fe-V}\) was -0.015 to -0.724. The V element shows the enhancement effects for the Fe element. The greater the Fe content, the larger the enhancement effects. For V-Fe samples, \(A_{V,Fe}\) was -0.674 to 0.006. The Fe element shows the enhancement effects for the V element. The greater the V content, the smaller the enhancement effects. When Fe content was greater than 65%, the Fe element exhibited a slight absorption effect for the V element.

![Figure 1](Image)

**Figure 1.** The ordinate represents the binary influence coefficient \(A_{V,Fe}(●)\), and the abscissa represents the V content; while the ordinate represents the binary influence coefficient \(A_{Fe,V}(○)\), and the abscissa represents the Fe content.

In Table 2, \( \mu_V \) was 427.00 cm\(^2\)·g\(^{-1}\) for the Fe element. In this case, the fluorescence of Fe was obviously aborted by the V element. In addition, the fluorescence intensity of V increased through its second fluorescence. Similarly, for the V element, \( \mu_V \) was 148.00 cm\(^2\)·g\(^{-1}\) and \( \mu_V \) was 98.20 cm\(^2\)·g\(^{-1}\). In this case, the Fe element produces scattering effects for the V element. Moreover, these slight enhancement effects were exhibited for the Fe element.

For the Ti-V samples (Fig. 2), the binary influence coefficients were quite negative. \(A_{Ti,V}\) was -1.200 to -0.990. The V element exhibited enhancement effects for the Ti element. The greater the Ti
content, the smaller the enhancement effect. For V-Ti samples, the binary influence coefficients were also quite negative. $A_{V,Ti}$ was -1.113 to -1.315. The Ti element exhibited enhancement effects for the V element. The greater the V content, the larger the enhancement effects.

![Figure 2](image)

Figure 2. The ordinate represents the binary influence coefficient $A_{Ti,V}$ (●), and the abscissa represents the Ti content; while the ordinate represents the binary influence coefficient $A_{V,Ti}$ (○), and the abscissa represents the V content.

According to Figure 2, with the gradient change in the primary base, the binary influence coefficients appear in a slightly convex curvature. The reason for this is because the initial emitted fluorescence of the Ti element had strong absorption for coherent and incoherent scattering.

For the Fe-Ti samples (Fig. 3), the binary influence coefficients are quite negative. $A_{Fe,Ti}$ was -1.138 to -1.082. The Ti element exhibited enhancement effects for the Fe element. The greater the Fe content, the smaller the enhancement effects. For the Ti-Fe samples, the binary influence coefficients were also quite negative. $A_{Ti,Fe}$ was -1.112 to -1.094. The Fe element also exhibited enhancement effects for the Ti element. The greater the Ti content, the smaller the enhancement effects.

In Table 2, for the mass absorption coefficient, the Fe element was 386.00 cm$^2$·g$^{-1}$, which was greater than the Ti element (120.00 cm$^2$·g$^{-1}$). For these reasons, the probability of photoelectric effects induced by the Fe element was less than that induced by the Ti element. Therefore, the secondary fluorescence of the Ti element was not obvious. Similarly, for the Ti element, the impact of Fe was mainly the scattering effect, rather than the photoelectric absorption effect. Therefore, the curve in Figure 3 had no obvious concave form.
Figure 3. The ordinate represents the binary influence coefficient $A_{Fe-Ti}$ (●), and the abscissa represents the Fe content; while the ordinate represents the binary influence coefficient $A_{Ti-Fe}$ (○), and the abscissa represents the Ti content.

5. **Correction**

In Figures 1, 2 and 3, $A_{ij}$, $C_i$ and $\mu_s$ were closely correlated. This shows that $A_{ij}$ cannot be regarded as a constant when analyzing the wide range content of samples. The relationship between $A_{ij}$ and $C_i$ was nonlinear. This study applied a mathematical fitting model to correct the matrix effects in these pseudo-binary samples.

In Section 3, $C_i$ and $A_{ij}$ satisfied the following exponential relationship, as presented in Equation (12).

$$C_i = A_1 - A_2 \exp(-kA_{ij})$$

(12)

In Equation (12), the parameters of the fitting equation such as $A_1$, $A_2$, $k$ and $R^2$ are listed in Table 3.

Table 3. Parameters of Equation (12) and goodness-of-fit

| $A_{ij}$     | Coefficient of the Eq. (12) | Goodness of fit |
|--------------|----------------------------|-----------------|
|              | $A_1$                     | $A_2$           | $k$      | $R^2$  |
| $A_{V,Fe}$   | 1.34737                   | 2.11232         | 0.00828  | 0.99958|
| $A_{Fe-V}$   | 0.76323                   | 0.74451         | -0.00985 | 0.99950|
| $A_{V,Ti}$   | -1.05259                  | 0.05216         | -0.02937 | 0.99722|
| $A_{Ti-V}$   | -0.94392                  | 0.29929         | 0.03118  | 0.99935|
| $A_{Ti-Fe}$  | -1.09068                  | 0.02460         | 0.02859  | 0.97625|
| $A_{Fe-Ti}$  | -1.30470                  | -0.16303        | -0.00446 | 0.99895|

This study corrects the matrix effects of the Fe-Ti samples using Equation (12). The results are shown in Figures 4 and 5.
Figure 4. Fe element concentrations in Fe-Ti sample alloys plotted against concentrations calculated from uncorrected Fe intensities (%). Note the maximum absolute and relative errors.

Figure 5. Fe element concentrations in Fe-Ti sample alloys plotted against concentrations calculated using \( A_{Fe-Ti} \) and Equation (12). Note the maximum absolute and relative errors.

In Figures 4 and 5, the maximum absolute error decreased from 5.92% to 0.27%, and the relative error decreased from 14.84% to 0.66%. This means that the fitting method of the correction for matrix effects in pseudo-binary samples was available. Similarly, this fitting method may be applied to other samples.

5. Conclusions
The method in this study can be an effective way to correct matrix effects in pseudo-binary samples. The binary influence coefficient is a significant parameter to analyze the absorption or enhancement...
effects. The mathematical fitting model can be used to correct matrix effects. This analytic method can be applied to other samples, and become an effectual manner for matrix effects correction in XRF analysis. However, the exponential fitting correction method is only a simple application for the matrix effect correction in pseudo-binary samples, and needs to be improved for practical applications.

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