

Validity evaluation of SQX analysis results

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Abstract

Standardless FP analysis can easily calculate analytical values, but there is no established method for assessing them. Consequently, their reliability may decrease if appropriate sample models and corrections are not set. One approach to address this issue is by comparing the Compton scattering X-ray intensity, converted from the theoretical Compton scattering X-ray intensity (calculated from the analytical value), to the measurement intensity scale (hereinafter, “theoretical scattering intensity”) with the actual measured Compton scattering X-ray intensity (hereinafter, “measured scattering intensity”). In this paper, we introduce the method and show the effectiveness for the validity evaluation of SQX analyses.

1. Introduction

X-ray fluorescence analysis is a relative analysis, where a calibration curve is made and stored in advance using standard materials. Daily routine analysis is then carried out based on this calibration curve. However, analyses without calibration curves arise when measurements are required for non-routine requests or research and development. These include the inability to obtain standard materials corresponding to the unknown samples, or having only one or two samples, even if such standard materials can be acquired, thereby making it impossible to create the calibration curves. Accurately judging the elements and their content ratios that constitute these samples is critical.

Given these demands, the fundamental parameter method⁽¹⁾ can be used to perform elemental analysis of unknown samples using the detected elements obtained from the qualitative analysis and the built-in sensitivity library of the instrument. This method is called the standardless Fundamental Parameter analysis⁽²⁾ (standardless FP analysis), or Scan Quant X (SQX), due to the fact that standard samples are not used.

This analysis method is commonly used due to the ease of obtaining analytical values; however, no indicator serves as the standard for the validity of the obtained analytical values. Therefore, judging whether the analysis result is obtained by a correctly set sample model or various corrections is required.

To solve this issue, a method is proposed for comparing the theoretical scattering intensity with the measured scattering intensity, which is then applied in practice to demonstrate its effectiveness.

2. Compton scattering X-ray

Compton scattering X-rays are generated by X-rays from an X-ray tube interacting inelastically with a sample. Its intensity varies according to sample components, especially the light element concentration.

Figure 1 shows a qualitative chart comparison of quartz glass (SiO₂) and metallic iron near Rh-K α -Compton. Quartz glass is primarily composed of light elements Si (silicon) and O (oxygen), and has a higher intensity of Compton scattering X-rays than metallic iron, which is primarily composed of the heavy element Fe (iron). The intensity of Compton scattering X-rays is generally closely related to the concentration of the light elements contained, and a higher scattered radiation intensity is achieved by increasing the amount of light element components.

3. Compton fit coefficient

3.1. What is the Compton fit coefficient?

This paper refers to the ratio of the theoretical scattering intensity obtained from the SQX analysis results to the measured scattering intensity as the Compton fit coefficient. A coefficient closer to one indicates a higher agreement between the analysis results and the measured data.

$$\text{Compton Fit coefficient} = \frac{I_T}{I_M}$$

I_T : Theoretical scattering intensity

I_M : Measured scattering intensity

3.2. Compton fit coefficient interpretation

The following is a guideline for interpreting the Compton fit coefficient for measured data.

$$\geq 0.9 \leq X \leq 1.1$$

The theoretical scattering intensity is consistent with the measured scattering intensity, indicating that the SQX analysis results are valid.

$$\geq X < 0.9$$

The theoretical scattering intensity is smaller than the measured scattering intensity. A small coefficient indicates that the effect of light element components

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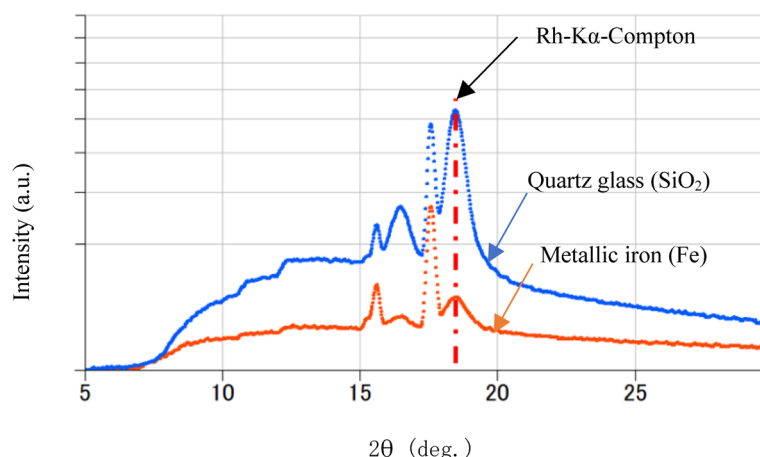


Fig. 1. Comparison of the qualitative charts of quartz glass (SiO_2) and metallic iron near the Rh-K α -Compton region (Crystal-detector: LiF(200)-SC).

on the analysis results is small (i.e., the theoretical scattering intensity is small), and there is a high possibility that information on light elements and ultralight elements is missing from the SQX calculation results.

➤1.1 < X

The theoretical scattering intensity is higher than the measured scattering intensity. A large coefficient indicates that the effect of light element components on the analysis results is high (i.e., theoretical scattering intensity is large), and there is a high possibility that information on light elements and ultralight elements is overestimated.

4. Applicable devices and calculation parameters

The Compton fit coefficient calculation function can be used with three models: ZSX PrimusIV, ZSX Primus IVi, and ZSX Primus III NEXT. However, the SQX scattering FP method (option) is required to use this function.

The Compton fit coefficient can be calculated in SQX calculation if the following conditions are met.

- Sample types: Powder, polymer, liquid (liquid samples are only compatible with tube below type ZSX Primus IVi)
- Balance setting: Must be set to a mode other than “estimate.”
- Sample size: Requires information on weight, height, and bottom size (diameter or area).
- Measurement diameter: Must be $\phi 30$ mm or 20 mm.

The following precautions should be observed when calculating the Compton fit coefficient:

- Ensure that the sample smoothly fits the analysis surface with a measurement diameter of $\phi 30$ mm or 20 mm
- Information on scattered radiation is utilized from the sample, therefore, ensure that the sample is positioned to prevent scattered radiation from any other materials. In particular, using a sample holder or double pellet method for samples with finite thickness

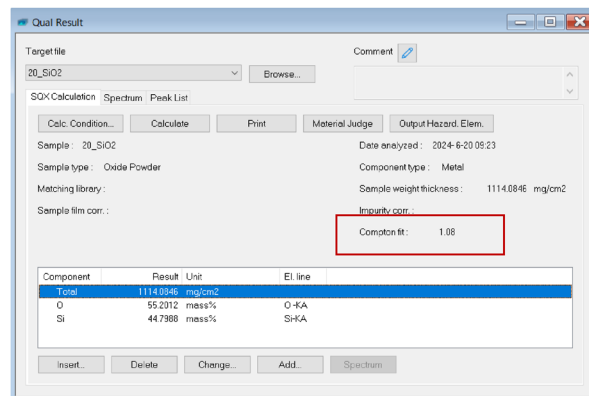
may result in scattered radiation from sources other than the measurement sample, leading to errors. Thus, caution is essential in such cases.

- Ensure that the analysis sample is homogeneous, given that this is an FP method.

5. Implementation example

5.1. Compton fit coefficient display screen

The coefficients are displayed in the “Compton fit” section on the SQX calculation tab screen of the analysis results.



5.2. Example of comparison of Compton fit coefficients

5.2.1. Example of application to quartz glass

Quartz glass (SiO_2) is a simple compositional material that comprises of two elements, Si and O, making it easy to intuitively understand how the Compton fit coefficient varies with the changes in the sample model when calculating analysis data. The standard values for this sample are 46.75% mass% Si and 53.25% mass% O. SQX calculation was carried out under the following three conditions, and the resulting Compton fit coefficients were compared. Table 1 compares the SQX analysis results and the Compton fit coefficients. It should be noted that the measured sample thickness information must be input to calculate the Compton scattering

Table 1. SQX analysis values and Compton fit coefficients.

Element/component	O	Si	SiO ₂	Compton fit coefficient
Standard value (unit)	53.25 (mass%)	46.75 (mass%)	100 (mass%)	
Setting 1	54.01	45.99	—	1.06
Setting 2	—	—	100	1.03
Setting 3	—	100	—	0.25

intensity. The actual sample thickness was measured using a caliper, and a thickness of 3 mm was used as the input value.

〈Example of sample model settings〉

- Setting 1: Component form: Model containing Si (analysis line Si-K α) and O (analysis line O-K α)
- Setting 2: Component form: Model containing only SiO₂ (analysis line Si-K α)
- Setting 3: Component form: Model containing only Si (analysis line Si-K α)

Setting 1 is a sample model that uses Si-K α as the analysis line for the Si concentration and O-K α as the O concentration. The obtained Compton fit coefficient is 1.06, which indicates that the theoretical scattering intensity and the measured scattering intensity are in good agreement.

Setting 2 is a sample model for determining the SiO₂ (silicon dioxide) concentration. The Compton fit coefficient is 1.03, which indicates that the theoretical scattering intensity calculated with SiO₂ at 100 mass% aligns well with the measured scattering intensity.

Meanwhile, setting 3 is an example of an incorrect sample model setting, where the sample SiO₂ contains only Si. The Compton fit coefficient is significantly small, at 0.25, indicating that O present in the sample is not considered as an element to be analyzed. Consequently, the theoretical scattering intensity is significantly smaller than the measured scattering intensity, since O is not considered. The analysis result further demonstrates that Si concentration of 100 mass% is an inappropriate analysis value.

5.2.2. Example of application to samples influenced by thickness

An example of applying this method to Cd analysis in polymers describes the influence of sample thickness. Given the high energy of the analysis line in the analysis of heavy elements in polymers, the analysis depth is deep and influenced by the sample thickness. Therefore, it is essential to accurately determine the sample size and to perform thickness effect corrections.

A disk-shaped sample (diameter 40 mm, weight 2.2 g, thickness 2 mm) of cadmium-containing polyethylene sample (VDA004/IRMM) was used. Table 2 shows a comparison of the cadmium analysis value and the Compton fit coefficient for the following sample model setting example. The balance component (non-measured component) was CH₂, and the measured sample thickness of 2 mm was used as a fixed value for

Table 2. SQX analysis value and Compton fit coefficient.

Element/component	Cd	CH ₂	Compton fit coefficient
Standard value (unit)	407 (ppm)	Balance	
Setting 1	403	Balance	0.96
Setting 2	854	Balance	0.46

calculating the theoretical scattering intensity.

〈Example of sample model settings〉

Setting 1: Case where sample size setting is correctly set (diameter 40 mm, weight 2.2 g)

Setting 2: When sample weight in the sample size setting is set incorrectly to 1 g (diameter 40 mm, weight 1 g)

The sample size information is set correctly in setting 1, so the Compton fit coefficient is close to one. Therefore, the analysis value of Cd (cadmium) obtained is judged to be close to the standard value.

Meanwhile, the Compton fit coefficient for setting 2 is 0.46, which is much smaller than one, and this result suggests that the theoretical scattering intensity calculated from the analysis results is smaller than the measured scattering intensity (i.e., the amount of adhesion per unit area (g/cm²) is small). Therefore, the estimated analytical value of the cadmium concentration in the polymer is 854 ppm, nearly double the standard value of 407 ppm. However, due to the significant discrepancy in the Compton fit coefficient, this analytical value is judged to be incorrect.

5.2.3. Example of applications including non-measured elements/components

5.2.3.1. Measuring powdered samples

This section presents a measurement example of lithium phosphate (Li₃PO₄) as a powder reagent containing Li (lithium). A complete qualitative analysis was carried out with the measurement element range of B to Cm. The detected elements in this element range are O and P (phosphorus). Table 3 compares the analytical values and Compton fit coefficients for the following sample model setting example.

〈Example of sample model settings〉

Setting 1: Model containing the two elements O and P

Setting 2: Model containing the three elements Li, O, and P, with Li as the input fixed element

In setting 1, only O and P were detected as the primary components. Hence, the Compton fit

Table 3. SQX analysis values and Compton fit coefficients.

Element/component	Li	O	P	Compton fit coefficient
Standard value (unit)	17.98 (mass%)	55.27 (mass%)	26.75 (mass%)	
Setting 1	—	66.0	34.0	0.73
Setting 2	17.98 (fixed value)	55.0	27.0	0.87

coefficient for the sample model containing only these two elements was 0.73, indicating that the theoretical scattering intensity calculated from the analytical values of the two elements was smaller than the measured scattering intensity. In other words, given the range of the measured elements, this indicates that elements below Be (beryllium) were present in the sample, suggesting that the analytical values for these two elements may be unreliable.

In setting 2, the sample was lithium phosphate (Li_3PO_4). Hence, Li was added as a non-measured element, and its content was set as a fixed value (standard value was used) and recalculated. Results showed that the theoretical scattering intensity increased, with the Compton fit coefficient improving from 0.73 to 0.87, which is close to the acceptable value of 0.9 to 1.1. This suggests that the reliability of the obtained analysis value is high, and the O and P contents are also close to the standard value.

5.2.3.2. Measuring liquid samples

Measuring the liquid sample using the liquid method (direct method) requires pouring the liquid directly into a sample cell with a sample film and performing the measurement under a gas atmosphere with helium (or nitrogen gas). Therefore, elements below oxygen are not measured, and the solvent information must be correctly set as a non-measured component.

A sample cell lined with 6 μm polypropylene film was filled with 5 g of 1000 ppm Zn (zinc) atomic absorption solution, and SQX analysis was carried out under a helium atmosphere. The detected element with the measurement element range of F to Cm was Zn. Table 4 shows a comparison of the SQX analysis values and Compton fit coefficients for each of the sample model settings below.

〈Example of sample model settings〉

Setting 1: Case where the solvent is set to H_2O (water)

Setting 2: Case where the solvent is set to CH_2 (paraffin oil)

Setting 1 involves using H_2O as the solvent for the sample model, resulting in a Compton fit coefficient

Table 4. SQX analysis values and Compton fit coefficients.

Element/component	Zn	H_2O	CH_2	Compton fit coefficient
Standard value (unit)	1000 (ppm)	Balance	Balance	
Setting 1	1065	Balance	—	0.93
Setting 2	443	—	Balance	1.20

of 0.93. This indicates that the theoretical scattering intensity calculated from the analysis values are in good agreement with the measured scattering intensity. This suggests that the analysis value of Zn is accurate and consistent with the standard value.

Meanwhile, setting 2 involves using CH_2 (paraffin oil) as the solvent type, resulting in a Compton fit coefficient of 1.2. This indicates that the theoretical scattering intensity calculated from the analysis results is higher than the measured scattering intensity.

This signifies that the coexisting element components of the calculated sample model contain more light elements than the actual sample results, leading to less absorption of the Zn- $K\alpha$ analysis line. Consequently, the Zn content is estimated lower than the actual content, resulting in a significant error of 443 ppm compared to the standard value of 1000 ppm.

6. Summary

When performing SQX analysis, a standardless FP analysis, the introduction of the Compton fit coefficient—defined as the ratio of the theoretical scattering intensity calculated from the SQX analysis results to the measured scattering intensity—enables easier evaluation of the validity of the SQX analysis values, sample model settings, and various correction methods.

References

- (1) Kohno, H.: *Advances in X-ray Analysis* **19** (1988), 307, 328
- (2) X-ray Fluorescence Analysis Handbook, “Standardless FP Analysis” (2023), pp. 125–131