Quantitative Analysis of Crystalline Silica by XRD

Kaho Hamada*, Miki Kasari*, and Keigo Nagao*

Abstract

Regulations on crystalline silica have been becoming increasingly strict worldwide and, in Japan, it has been designated as a material subject to risk assessment. Therefore, it is essential to confirm the applicability of the regulatory cut-off value (0.1%) and to appropriately control the amount of crystalline silica in, for example, glass, ceramics, or bricks based on this threshold. As a result, the demand for quantitative analysis is increasing. However, current regulations do not specify an analytical method for determining silica content in powders.

In this technical note, we propose the use of a calibration curve method employing an X-ray diffractometer for the quantification of crystalline silica. We also compare different diffractometers and slit optics configurations, and consider the optimal approach for accurate quantification.

The limits of detection for three crystalline silica samples were all below 0.1%, the regulatory cut-off value. The quantitative results obtained using both a 0–100% calibration curve (based on a standard sample) and a 0–1% calibration curve (based on a matrix-matching method) showed good agreement with the prepared concentrations, demonstrating the effectiveness of the calibration curve method.

1. Introduction

Crystalline silica is the common name for crystallized silicon dioxide (SiO_2), a natural mineral. It can be found in materials such as sand, stone, concrete, and mortar, materials that are used for the manufacture of products such as glass, ceramics, and bricks(1). However, inhaling crystalline silica may cause health problems such as silicosis, lung cancer, and kidney disease(2). Consequently, regulations on crystalline silica have been strengthened in many countries around the world. In the United States, if a product contains 0.1% (hereafter, “%” means mass fraction) or more of crystalline silica, the Hazard Communication Standard (HCS) of the Occupational Safety and Health Administration (OSHA) of the Department of Labor states that it is required to include that information in a Safety Data Sheet (SDS) and to display a warning on the label indicating carcinogenicity (2). The European Union (EU) regulates the use of chemicals in its Registration Evaluation Authorisation and Restriction of Chemicals (REACH) and Classification, Labelling and Packaging (CLP) regulations, setting 0.1% as the cut-off value (3)–(6).

In Japan, the Ministry of Health, Labor and Welfare (MHLW) has tightened regulations on crystalline silica, requiring the issuance of SDSs, labeling, and the storing of work records. The cut-off value is also 0.1% (7). Since there are many materials containing 0.1% or more crystalline silica, there is a growing demand for methods to quantify low concentrations of crystalline silica. However, the quantitative method has not been specified. X-ray diffraction is effective for the analysis of crystalline silica because it is non-destructive and enables quantitative analysis with differentiation of crystal polymorphs.

In this technical note, we will describe the results of quantitative analysis and the optimal optical system for three types of crystalline silica contained in calcium carbonate.

2. Quantitative Method for Crystalline Silica

2.1. Calibration curve method and spike recovery rate

First, in the calibration curve method, the analyte and matrix are mixed to prepare samples with different concentrations. Each sample is submitted for measurement and the diffraction intensity of the analyte is obtained. The regression equation between concentrations and diffraction intensities is then used for quantitation. The calibration curve method by X-ray diffraction has the following advantages:

①The concentration of the analyte relative to the sample weight is accurately calculated even if the sample contains amorphous or unidentified crystalline phases.

②The method uses only one peak, is simple to process, and is highly accurate. In a method such as quantitative analysis by the Rietveld method, where the total content of crystalline phases is 100%, the quantitative accuracy of the other phases affects the quantitative value of the analyte.

③The acquisition of integrated intensities is basically not profile fitting, but peak integration, which integrates intensities in a defined 2θ range. Therefore, even if the intensity is low and the shape of the peak is corrupted, the calibration curve method enables accurate quantification of trace components near the limit of detection (LOD).

④In a concentration range where the linearity of the calibration curve is high, if the calibration curve has

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* Application Laboratories, Product Division, Rigaku Corporation.

only two points, 0% and one other point, the 0% point is surely located on the regression line. Therefore, accurate quantification can be performed from low to high concentrations.

In this study, two calibration curve methods were used for the quantification of crystalline silica: the first is a 0–100% calibration curve. A two-points calibration curve (0–100%) was prepared with the crystalline silica reagent as 100% sample and the matrix component reagent as 0% sample. The 0–100% calibration curve does not require mixing of reagents for the calibration curve, which makes the quantitative analysis easier. However, if the mass absorption coefficient of the matrix component differs from that of crystalline silica, the diffraction intensity from low concentrations of crystalline silica will decrease or increase due to the difference in absorption by the matrix component. As a result, the quantitative value cannot be calculated correctly. Therefore, it is effective to correct the quantitative value by using the "spike recovery ratio (SRR)". The SRR is calculated from equation (1).

$$SRR\left[\%\right]=\frac{w_{after}-w_{before}}{w_{add}}\times 100 \tag{1}$$

Where w_{after} is the quantitative value after addition, w_{before} is the quantitative value before addition, and w_{add} is the concentration added. In the study, a sample spiking 1% crystalline silica was used to calculate the SRR, and the quantitative values were corrected.

The second is the 0–1% calibration curve method using the matrix matching method. The matrix-matching method is a quantitative technique in which a standard sample is prepared to match the matrix of an unknown sample. The advantage is that the intensity correction calculation due to matrix components is not necessary and can be performed as is. On the other hand, the disadvantages are as follows: It requires a reagent with a matrix component of high purity that contains either no crystalline silica as an impurity or a negligible amount. In addition, crystalline silica must be accurately mixed with the matrix component to create a calibration curve.

2.2. Sample for calibration curve

Calcium carbonate (made by Kojundo Chemical Laboratory Co., Ltd., Japan) was used as the matrix. For standard samples, quartz (made by Kojundo Chemical Laboratory Co., Ltd., Japan), tridymite (Tri.31) (made by Japan Association for the Study of Fiber Materials), and cristobalite (1879b) (made by the National Institute of Standards and Technology (NIST), USA) were used, respectively. These materials were wet-mixed to obtain concentrations of 0.1, 0.2, 0.5, and 1% of crystalline silica in calcium carbonate.

2.3. Limit of detection (LOD) and limit of quantification (LOQ)

Statistical processing is necessary because of statistical variation in X-ray counting. Since the detection limit corresponds to three times the standard deviation σ of the measured value, the LOD is calculated using equation (2)$^{(8)}$.

$$\mathrm{LOD}=\frac{3\times\sigma}{k} \tag{2}$$

where k is the slope of the calibration curve. σ is often calculated by repeating the measurement of one low-content sample about 10 times $^{(8)}$.

On the other hand, considering the repeatability and reliability of the quantitative values obtained, LOQ is defined as 10 times the standard deviation σ as in equation (3)$^{(8)}$.

$$\mathrm{LOQ}=\frac{10\times\sigma}{k} \tag{3}$$

3. Measurement and Analysis Conditions on an X-ray Diffractometer

3.1. Sample preparation

Sample molding was performed by the back-press method using the powder molding machine manufactured by Rigaku. The use of the powder molding machine can reduce human errors and make the sample preparation pressure uniform, suppressing eccentricity error and improving refill repeatability $^{(9)}$. A bottomless Al sample holder (φ24 mm) was used as the sample holder (Fig. 1a). This sample holder can be mounted on an automatic sample changer (ASC). This enables more efficient and simplified measurements. ASC-10 (for up to 10 samples) was used on SmartLab SE, an automated multipurpose X-ray diffractometer, and ASC-8 (for up to 8 samples) was used on MiniFlex, a benchtop X-ray diffractometer. If the sample is improperly prepared in the back-press method, material may fall from the holder during measurement, possibly contaminating the inside of the instrument or the ASC. In such cases, a sample dropout prevention lid (Fig. 1b) for the bottomless Al sample holder can be placed between the ASC and the sample holder to minimize contamination.

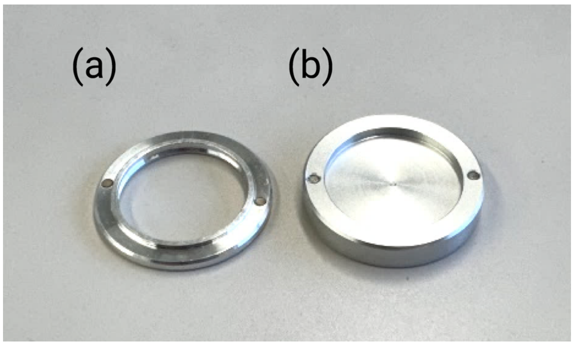

Fig. 1. Sample holder.
a: Bottomless Al sample holder (φ24 mm)
b: Sample dropout prevention lid for the bottomless Al sample holder

3.2. Measurement conditions

In this report, we measured the samples using two X-ray diffractometers, SmartLab SE and MiniFlex, with three different sets of optical conditions. The measurement 2θ range was set to 18.0–21.5° for tridymite, 21.0–23.0° for cristobalite, and 25.0–28.0° for quartz. The scan step was 0.02°. The scan speed was 0.5°/min and the three peaks were measured in approximately 45 minutes. Measurement conditions were the same as the three optics conditions described in section 3.2.1 to 3.2.3. It is usually desirable to select the strongest peak for each crystalline silica for the measurement range, but the strongest peak of tridymite is close to the diffraction peak of calcium carbonate; therefore, the measurement was performed by selecting the area around the second strongest peak. Three peaks detected in this research have broad peak widths due to small crystallite size, so the step width was set to the coarse value (0.02°).

3.2.1 SmartLab SE + BB optics + XSPA-400 ER

We measured samples using SmartLab SE at a tube voltage of 40 kV and current of 50 mA (2 kW). This system was equipped with XSPA-400 ER, a seamless multidimensional pixel detector$^{(10)}$, and the measurements were performed using Bragg-Brentano para-focusing optics (BB optics) (Fig. 2) without a multilayer mirror optical device$^{(11)}$. The detector was placed in a vertical orientation. A 5.0° wide receiving Soller slit, a larger aperture width than normal (30 mm in the 2θ direction), was used to allow the detector to receive more diffracted X-rays. The high energy resolution of the detector allows this optical system to obtain a measurement profile with a low background and a significant reduction of peaks caused by Kβ radiation.

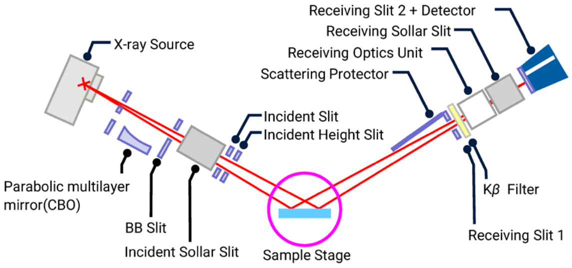

Fig. 2. Schematic diagram of BB optics

3.2.2 SmartLab SE + DB optics + D/teX Ultra250

This system is equipped with D/teX Ultra250, a high-resolution and high-speed 1D silicon strip detector. We used Bragg Brentano para-focusing optics (Fig. 3) using the monochromatic divergent beam obtained from a flat multilayer mirror using the CBO-α unit $^{(11)}$. This system is called DB (Divergent Beam) optics.

3.2.3 MiniFlex

X-ray output of MiniFlex was set to a tube voltage of 40 kV and current of 15 mA (600 W). This system was equipped with D/teX Ultra2, a high-resolution and high-speed 1D silicon strip detector, and measurements were performed using Bragg-Brentano para-focusing optics (Fig. 4). A Ni filter with a thickness of 38 μm was used as a Kβ filter.

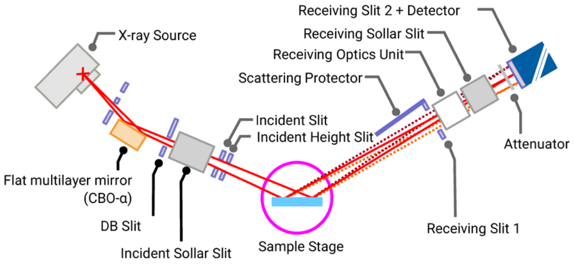

Fig. 3. Schematic diagram of DB optics

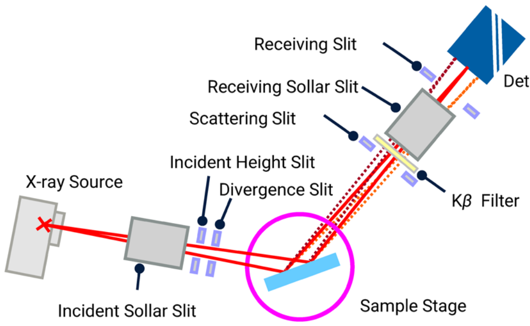

Fig. 4. Schematic diagram of MiniFlex optics

3.3 Analysis conditions

All analyses were performed using Rigaku's integrated X-ray analysis software, SmartLab Studio II (Powder XRD plug-in, quantitative analysis task) $^{(12)}$. Peak integration processing was performed to obtain the integrated intensity. The analysis range was defined as the range where the background can be linearly subtracted.

4. Results and discussion

Figures 5–7 show the profiles of each of the three crystalline silica species at each concentration using the SmartLab SE + BB optics. Figures 8–10 and 11–13 show the profiles by SmartLab SE + DB optics and MiniFlex, respectively. In each optical system, a peak of 0.1% silica could be detected. This indicates that even a benchtop X-ray diffractometer can detect low-concentration crystalline silica. On the other hand, with all optics, low concentrations of tridymite peaks (Figures 5, 8, and 11) tended to be less visible than the others; a slower scanning speed is desirable to improve the signal-to-noise ratio and to observe trace peaks more clearly.

Tables 1–3 show the LOD and LOQ for each crystalline silica using the 0–100% calibration curve for each optics. The LOD and LOQ are corrected for SRR. In most cases, detection at the regulatory cut-off value of 0.1% was successfully achieved.

The detection performance of trace constituents differed depending on the measurement optics. Tables

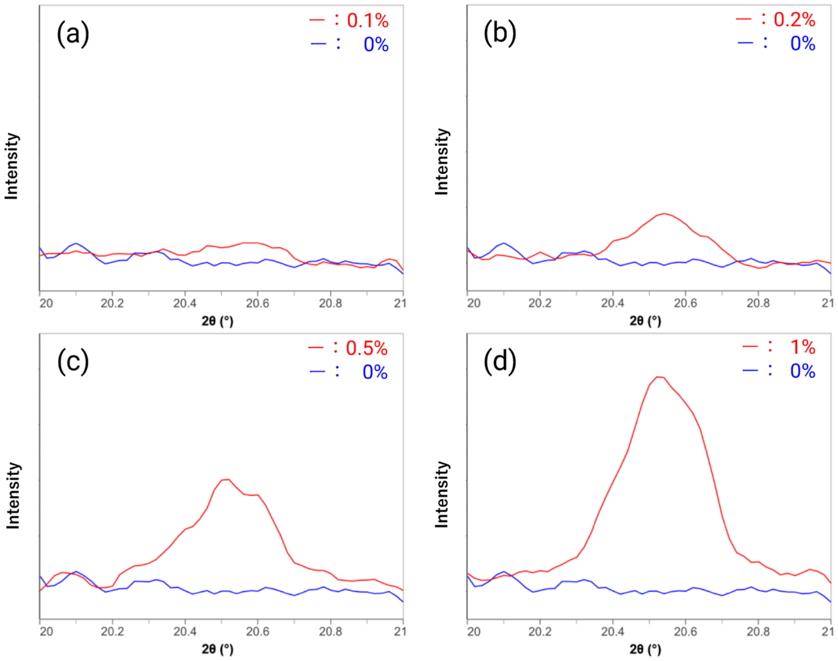

Fig. 5. Measurement profile of tridymite using BB optics.
(a) 0%, 0.1%, (b) 0%, 0.2%,
(c) 0%, 0.5%, (d) 0%, 1%.

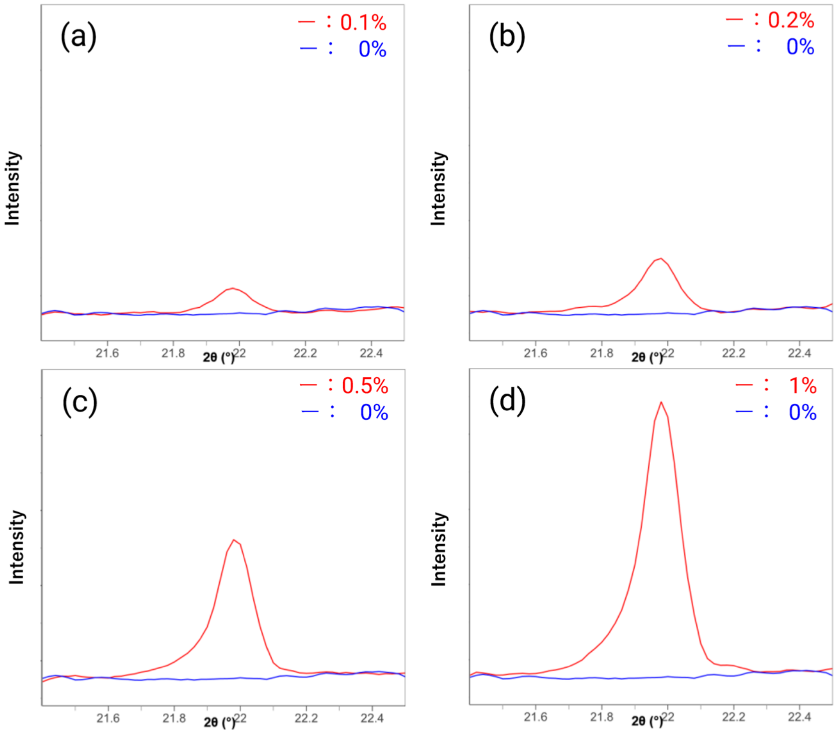

Fig. 6. Measurement profile of cristobalite using BB optics.
(a) 0%, 0.1%, (b) 0%, 0.2%
(c) 0%, 0.5%, (d) 0%, 1%.

1–3 show that the order of LOD is generally SmartLab SE+DB optics < SmartLab SE+BB optics < MiniFlex for all test materials, which means that the SmartLab SE+DB optics has the highest detection sensitivity. This is because the DB optical system is a para-focusing optic where X-rays are monochromatized on the incident side, thus suppressing the generation of fluorescent X-rays from the sample and providing high-intensity data. In the case of either optic, the LOD and LOQ can be improved by increasing the measurement time to obtain

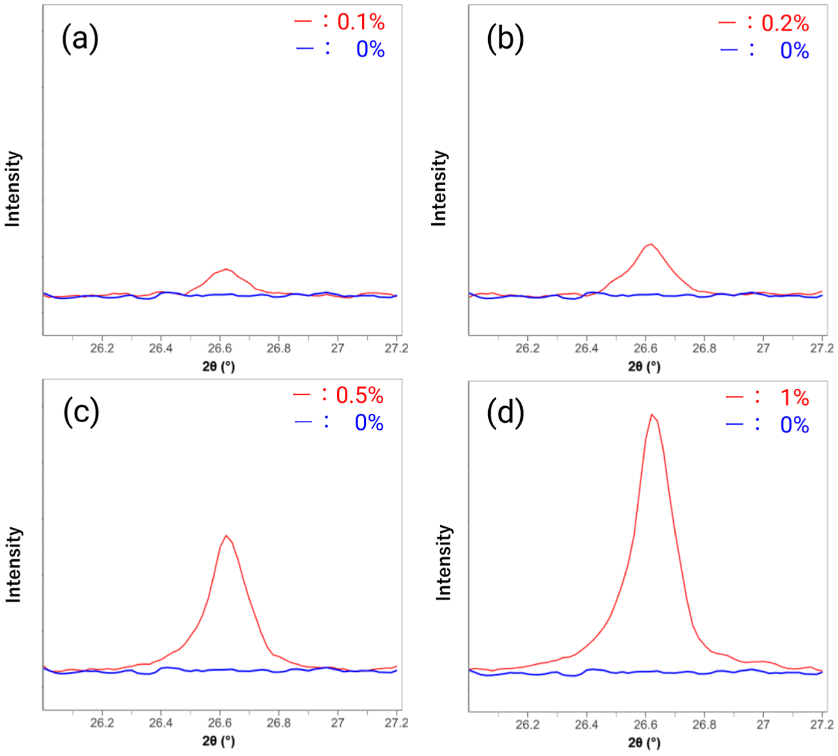

Fig. 7. Measurement profiles of quartz using BB optics.
(a) 0%, 0.1%, (b) 0%, 0.2%,
(c) 0%, 0.5%, (d) 0%, 1%.

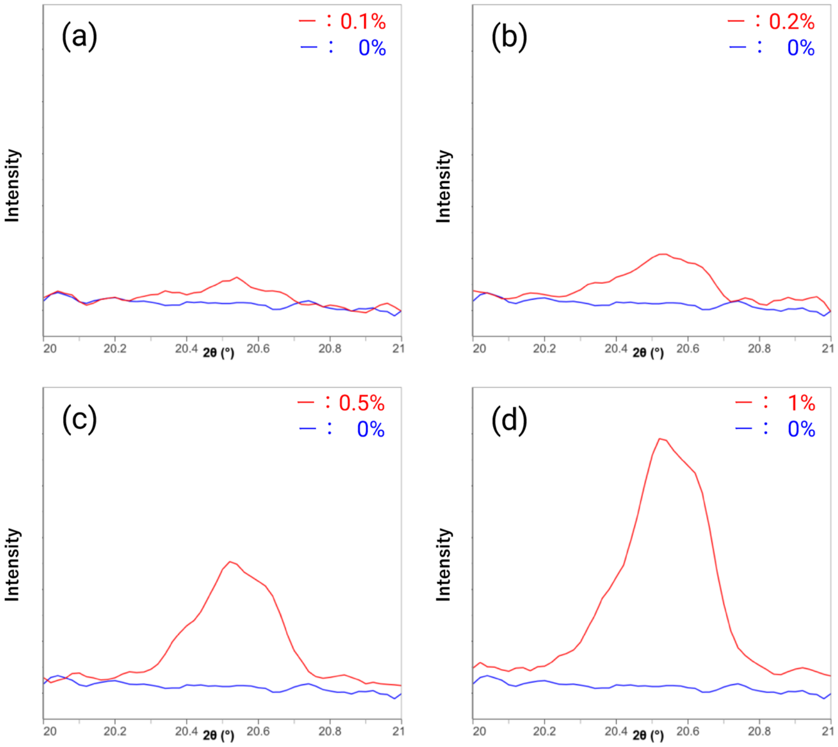

Fig. 8. Measurement profile of tridymite using DB optics.
(a) 0%, 0.1%, (b) 0%, 0.2%,
(c) 0%, 0.5%, (d) 0%, 1%.

a small σ according to equations (2) and (3).

Finally, two types of calibration curves were examined: 0–100% and 0–1% using the matrix matching method with SmartLab SE+DB optics, which achieved the lowest detection limit. Tables 4–6 show the LOD and LOQ for each crystalline silica using the 0–1%

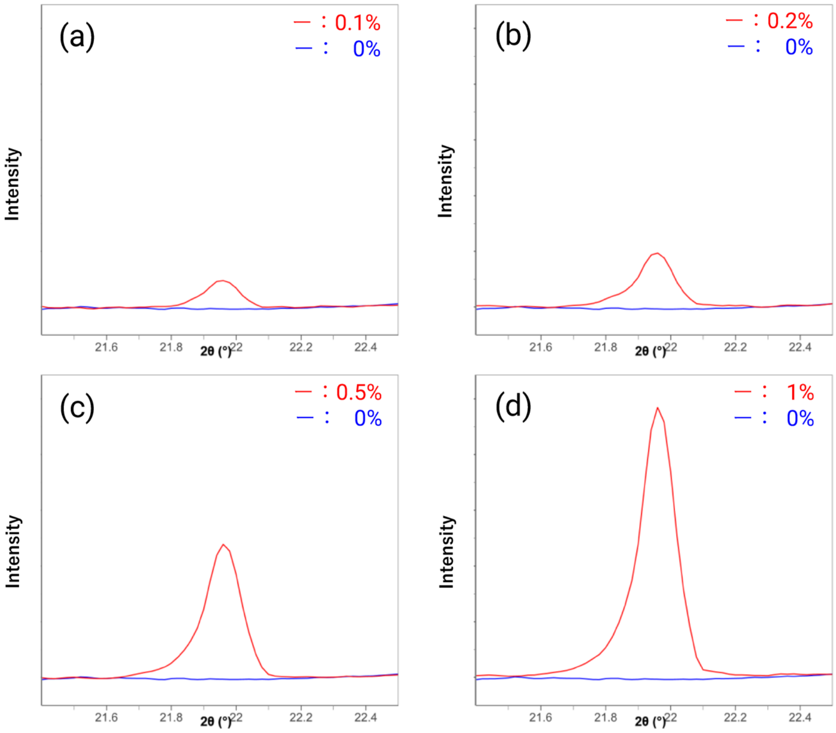

Fig. 9. Measurement profile of cristobalite using DB optics.
(a) 0%, 0.1%, (b) 0%, 0.2%,
(c) 0%, 0.5%, (d) 0%, 1%.

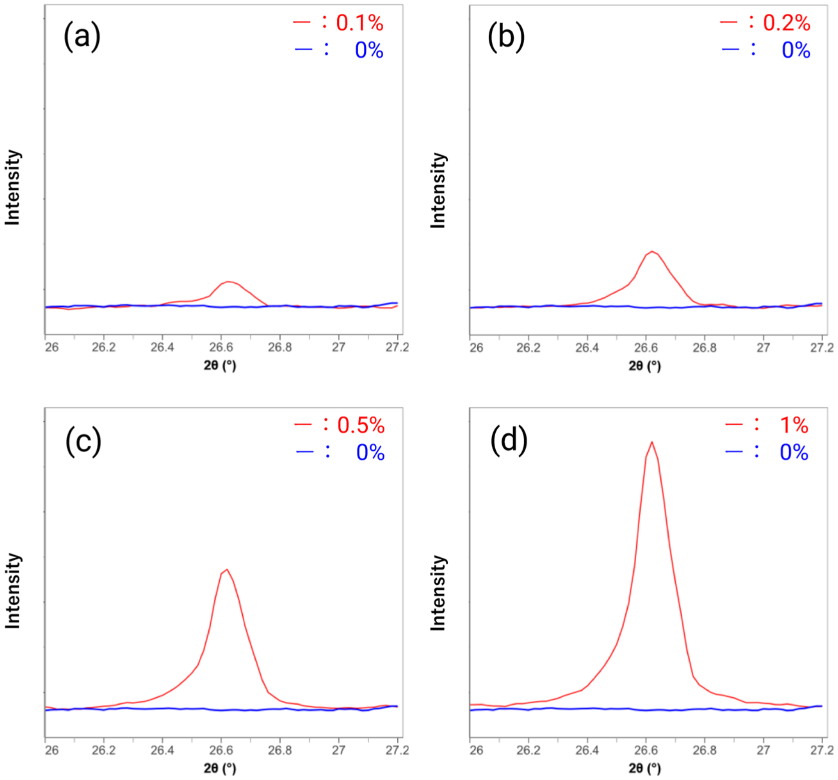

Fig. 10. Measurement profiles of quartz using DB optics.
(a) 0%, 0.1%, (b) 0%, 0.2%,
(c) 0%, 0.5%, (d) 0%, 1%.

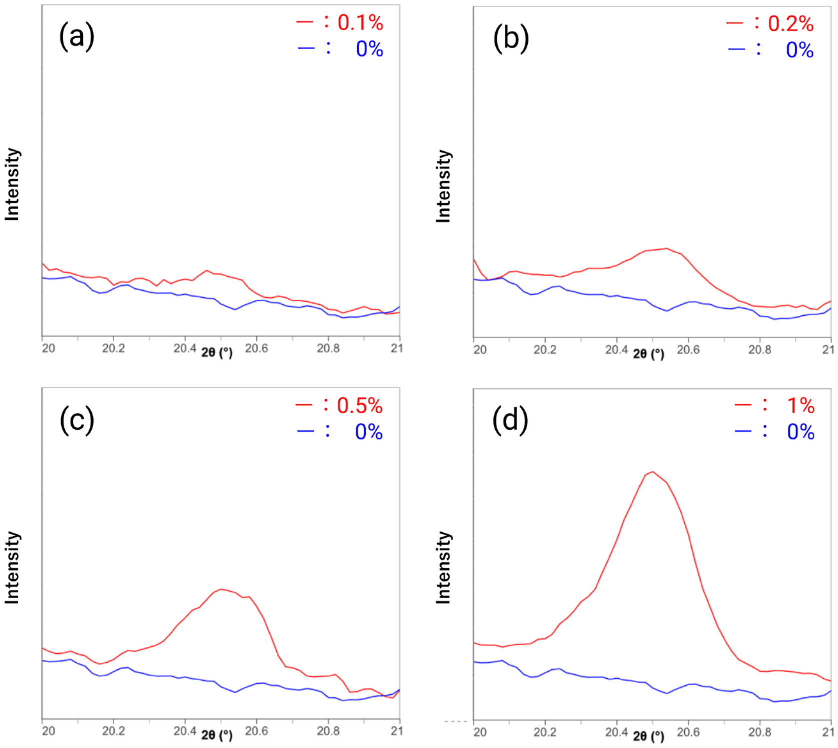

Fig. 11. Measurement profiles of tridymite using MiniFlex
(a) 0%, 0.1%, (b) 0%, 0.2%,
(c) 0%, 0.5%, (d) 0%, 1%.

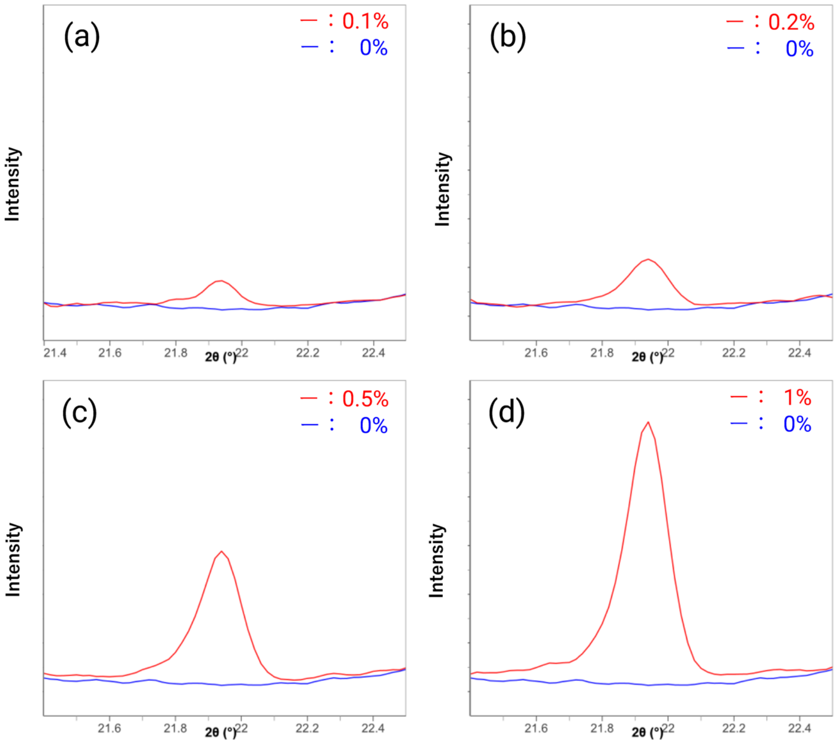

Fig. 12. Measurement profiles of cristobalite using MiniFlex.
(a) 0%, 0.1%, (b) 0%, 0.2%,
(c) 0%, 0.5%, (d) 0%, 1%.

calibration curve using each optic, and Tables 7–8 show the quantification results from each calibration curve. Compared to the results seen in Tables 1–3, the LOD and the LOQ were not affected by the differences in the calibration curves. The quantification results agreed well within the limits of errors compared to the prepared

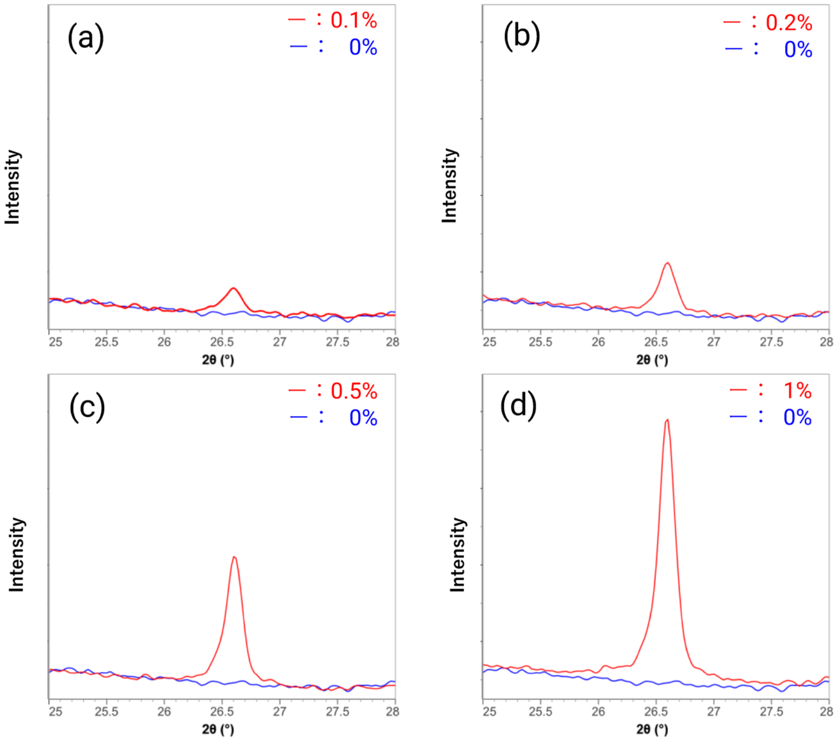

Fig. 13. Measurement profiles of quartz using MiniFlex.
(a) 0%, 0.1%, (b) 0%, 0.2%,
(c) 0%, 0.5%, (d) 0%, 1%.

Table 1. LOD and LOQ in calcium carbonate when using the 0–100% calibration curves on SmartLab SE+BB optics

	LOD[%]	LOQ[%]
Tridymite	0.10	0.32
Cristobalite	0.03	0.10
Quartz	0.07	0.23

Table 2. LOD and LOQ in calcium carbonate when using the 0–100% calibration curves on SmartLab SE+DB optics

	LOD[%]	LOQ[%]
Tridymite	0.08	0.27
Cristobalite	0.03	0.09
Quartz	0.03	0.12

Table 3. LOD and LOQ in calcium carbonate when using the 0–100% calibration curves on MiniFlex

	LOD[%]	LOQ[%]
Tridymite	0.17	0.58
Cristobalite	0.02	0.08
Quartz	0.04	0.14

Table 4. LOD and LOQ in calcium carbonate when using the 0–1% calibration curves on SmartLab SE+BB optics

	LOD[%]	LOQ[%]
Tridymite	0.10	0.35
Cristobalite	0.04	0.12
Quartz	0.06	0.21

Table 5. LOD and LOQ in calcium carbonate when using the 0–1% calibration curves on SmartLab SE+DB optics

	LOD[%]	LOQ[%]
Tridymite	0.08	0.27
Cristobalite	0.03	0.09
Quartz	0.04	0.12

Table 6. LOD and LOQ in calcium carbonate when using the 0–1% calibration curves on MiniFlex

	LOD[%]	LOQ[%]
Tridymite	0.17	0.58
Cristobalite	0.02	0.08
Quartz	0.04	0.14

values for all the calibration curves. It is important to correct the values from the 0–100% calibration curve results with the SRR obtained by quantifying 1% of silica in $CaCO_3$. The effect of X-ray absorption can be corrected, and it enables accurate quantification. In summary, the two calibration curve methods listed in this report are effective for quantitative analysis.

5. Conclusion

We have shown examples of the evaluation of crystalline silica using the X-ray diffraction method. By utilizing the calibration curve method, it is possible to determine trace amounts of crystalline silica with a high degree of accuracy.

In this analysis, the presence or absence of 0.1%

crystalline silica was confirmed. It was also found that the use of DB optics increased the detection sensitivity. If it is not possible to prepare a matrix component that does not contain crystalline silica, a calibration curve method called the "standard addition method" can also be applied. In this method, a pure analyte to be tested is added to the sample to create a calibration curve (13). However, this method is effective only when the background can be linearly subtracted (when the net intensity of the peak can be accurately calculated by background correction).

We are confident that, in the near future, the calibration methods described above will make a significant contribution to the evaluation of materials containing crystalline silica in accordance with regulatory requirements.

Table 7. Quantification results using 0–100% calibration curves

	Weighing value [%]	Quantification results [%]
Tridymite	0.1	0.1*
	0.2	0.2*
	0.5	0.52
	1.0	1.0
Cristobalite	0.1	0.1*
	0.2	0.18
	0.5	0.48
	1.0	1.0
Quartz	0.1	0.1*
	0.2	0.20
	0.5	0.48
	1.0	0.94

*···LOQ or less

Table 8. Quantification results using 0–1% calibration curves

	Weighing value [%]	Quantification results [%]
Tridymite	0.1	0.1*
	0.2	0.2*
	0.5	0.52
	1.0	1.0
Cristobalite	0.1	0.1*
	0.2	0.18
	0.5	0.47
	1.0	1.0
Quartz	0.1	0.1*
	0.2	0.21
	0.5	0.51
	1.0	1.0

*···LOQ or less

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