Making high speed, high resolution measurements using MiniFlex II+D/teX Ultra

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1. Introduction

The MiniFlex II benchtop XRD system is widely used in a variety of fields. Its small size, high angular performance and dependable design lend it the flexibility necessary for this range application. Over time, our users have started to place higher demands on the system. There has been diversification in the types of samples being measured, and laws and regulations have changed. For example, in asbestos analysis, it is necessary to detect trace phases of crystal in a short time. In order to respond to these requirements, Rigaku has made it possible to use the D/teX Ultra with the MiniFlex II. D/teX Ultra is a high-speed, one-dimensional X-ray detector that enables the MiniFlex II to perform high speed/high intensity measurement, obtaining higher angular and energy resolutions than previously possible. Using the D/teX Ultra, users can collect high quality data in a short time. This report details these new capabilities and provides examples of how they have been applied.

2. High speed, high sensitivity

Generally, the counting of X-rays has statistical fluctuation, and is associated with what is called "statistical error of counting". The statistical fluctuation is observed as noise on a profile, and this noise is smaller when the X-ray intensity is higher. Therefore, a profile based on data collected from high intensity X-rays looks smooth, making it easier to distinguish the smaller peaks. Furthermore, this high intensity profile makes it possible to accurately calculate peak positions, or areas that should be higher. Conventional systems typically require long measurement times to obtain high intensity profiles, but with the new system's high-speed and high-sensitivity, it is possible to collect high-intensity data in with a short measurement time.

Despite the small goniometer radius of 150 mm and low power requirements (30 kV and 15 mA), the intensity obtained by MiniFlex II is almost identical to the intensity obtained by high-end models. Moreover, the intensity obtained with D/teX Ultra is up to dozens of times greater than that obtained with a standard scintillation counter (SC). For further information, refer to the "New products" section of this issue[(1)].

[Example 1] Detection of 0.01 wt% crystal silica (SiO_2)

Recently, there is a growing recognition that crystal silica (free silica) dust should be considered to be a major cause of cancer. If the results of an analysis show that raw materials or products contain more than 0.1 wt% crystal silica, the Ministry of Health, Labor and Welfare in Japan requires that the results of the analysis be shown in a Material Safety Data Sheet (MSDS). Based on this regulation, there has been an increased demand for instruments able to perform quantitative analysis of crystal silica in a short time.

In simulated analysis, the quantitative analyses of 0.01–0.05 wt% of crystal silica in alumina (Al_2O_3) were performed by Kβ filter method at 0.2 deg/min. The results obtained with a SC are shown in Fig. 1, and with D/teX Ultra are shown in Fig. 2. The lower limit of detection with a SC is 0.05 wt%, while with D/teX Ultra it is 0.01 wt%. The data indicates that this benchtop XRD system meets and significantly exceeds the detection limit requirements for crystal silica.

[Example 2] Rietveld analysis of four inorganic crystal phases

In quantitative analysis, the calibration curve method used to be one of the more popular methods. In recent years, however, the quantitative analysis using the Rietveld method started to become more common based on improvements in computer processing power and software. The Rietveld method allows users to obtain quantitative values without calibration curves. Moreover, the Rietveld method has the ability to correct the effects of preferred orientation. When a sample shows preferred orientation, specific peaks appear to be stronger when measured. This is caused by pressure when layer compounds or needle like compounds press on the sample holder. So, the quantitative values obtained by the Rietveld method are more reliable than the calibration curve method.

There is a problem, however. In Rietveld method the profile fitting is performed over a wide angular range, meaning that the data has to be acquired over a wide angular range and at high intensity. The target for angular range is approx imately $2\theta = 5$–90 degrees with CuKα radiation, and the intensity should be 10,000 counts for the highest peak. To reach these targets, a conventional system requires very long measurement times. In this example, we tried to perform the quantitative analysis by Rietveld method in a shorter time with D/tex Ultra instead of SC.

The sample contained four inorganic crystal phases and was measured in about ten minutes. The profile was

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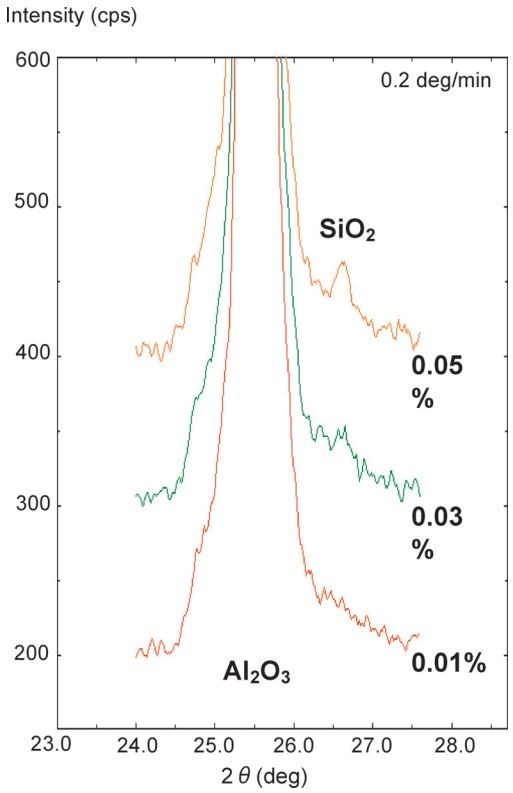

Fig. 1. X-ray diffraction profiles of crystal silica in Alumina with SC.
(The profiles are drawn with offset)

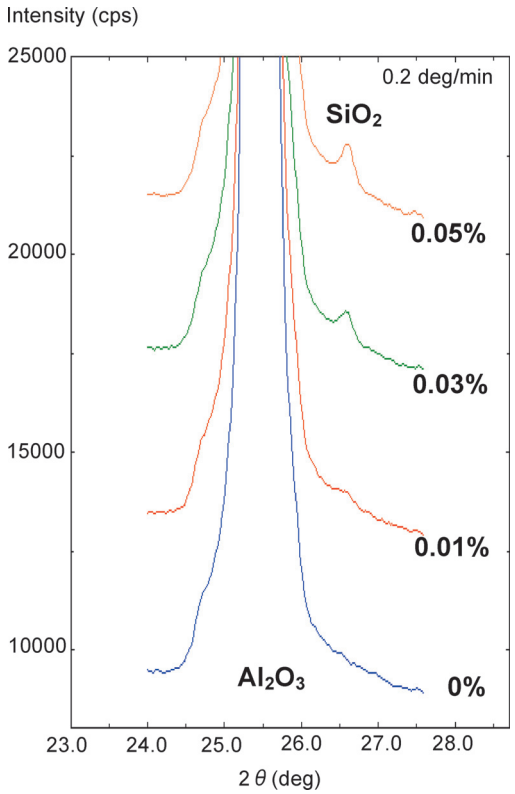

Fig. 2. X-ray diffraction profiles of crystal silica in Alumina with D/teX Ultra.
(The profiles are drawn with offset)

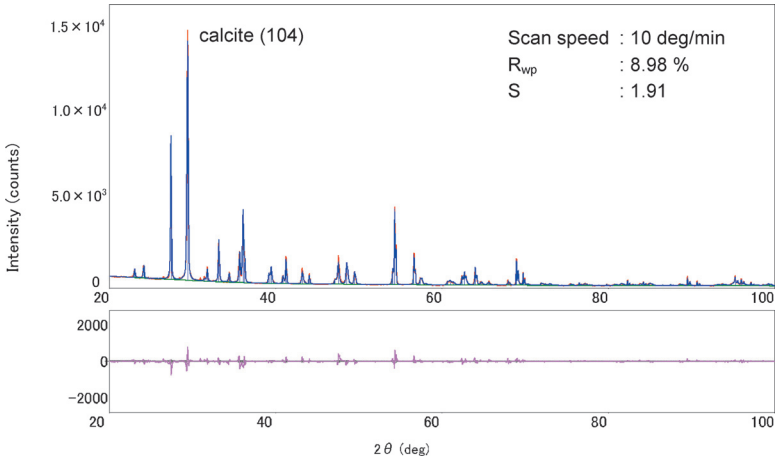

Fig. 3. Result of refinement by Rietveld method for the profile of four inorganic phase mixture.
(Measurement time: *ca.* 10 min)
(Measured profile: ▬, calculated profile: ▬, residual error: ▬)

Table 1. Result of quantitative analysis for four inorganic crystal phases (unit: wt %).

Crystal phase		Preparation	WPPF
Calcite	$CaCO_3$	43.7	43.3(4)
Rutile	TiO_2	37.3	38.0(2)
Hematite	Fe_2O_3	14.7	14.24(17)
Zincite	ZnO	4.3	4.49(13)

analyzed with using PDXL: Integrated X-ray Powder Diffraction software. The calculated data was well-matched at the measured data (Fig. 3), and the quantitative value well-matched at the prepared value (Table 1). Calcite ($CaCO_3$) which is contained in this sample is easily orientated at (104) when it pressed on the sample holder. But the results indicate that the effect of the preferred orientation was relieved with Rietveld method. The long time needed for advanced analysis has been eliminated, thus, it is now being performed in a short

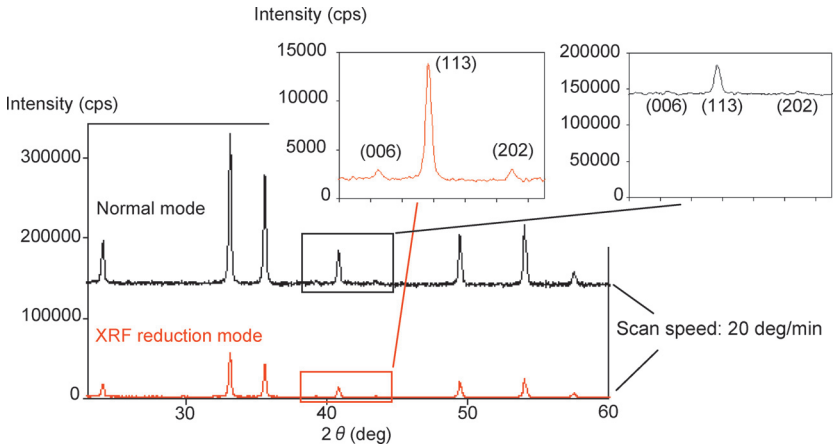

Fig. 4. The effect of the using XRF reduction mode.
(Sample: hematite. Measurement time: *ca.* 3 min)

time using benchtop XRD system with D/teX Ultra.

3. High angular resolution

If the sample contains many phases or the crystal structure is complicated, the peaks tend to overlap. For these kinds of samples, high angular resolution is required to separate the overlapped peaks. High angular resolution measurement makes the analysis of data collected from these samples much easier. For high angular resolution measurement using SC, the width of the receiving or soller slit is typically narrowed, but this has a side effect of decreasing peak intensity.

In the case of D/teX Ultra, each detecting strip collects angular information, so D/teX Ultra can achieve a high angular resolution without modifying the receiving slit. In addition, the intensity obtained by D/teX Ultra is dozens of times higher than that of an SC, so we can use narrow soller slit (options) for high angular resolution measurement.

4. High energy resolution

In general, if the sample contains elements which have high mass-absorption coefficients for the X-ray wavelength employed, the fluorescence X-rays will be emitted from the sample, resulting in higher and noisier background (baseline) on the profile. For example, if we measure a sample which contains iron using CuKα radiation, the high background noise makes it difficult or impossible to detect small peaks. In a conventional system, the user has to change the wavelength or attach an appropriate monochromator to reduce the influence of fluorescence in a conventional system.

D/teX Ultra has high energy resolution and the user can change the energy detection range from the software-side. The D/teX Ultra can be set to standard mode for normal samples, and can be put in XRF reduction mode when used to collect data from samples which emit fluorescence X-rays. XRF reduction mode enables to perform low background measurements without counter monochromator.

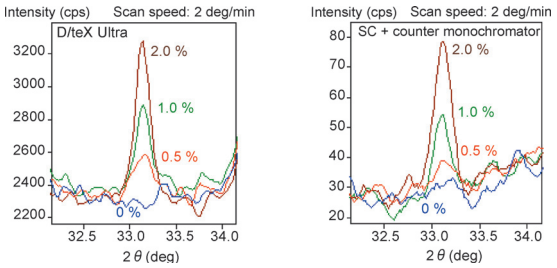

Fig. 5. Hematite (104) peaks in the magnetite.

[Example 3] Detection of small peaks in iron sample

Figure 4 shows a comparison of two hematite (Fe_2O_3) profiles, one measured in standard mode and the other in XRF reduction mode. Using XRF reduction mode, peak intensity/background intensity (P/B) ratio is improved, and the small peaks such as hematite (006) and hematite (202) can be seen clearly.

Figure 5 shows the hematite, Fe_2O_3 (104) peaks derived from very small amount of hematite, in magnetite, Fe_3O_4. The hematite content was 0.5, 1.0 and 2.0 wt%. While the SC was able to detect the 0.5 wt% hematite when using a counter monochromator, the intensity was low. With D/teX Ultra, the peak intensity for the same measurement time was about 40 times higher than the SC, and the 0.5 wt% hematite was clearly detected.

5. Conclusion

The combination of D/teX Ultra with the benchtop XRD system MiniFlex II results in an instrument capable of performing advanced analysis—a system that is competitive with the performance of existing high-end instruments. The capability for this system to detect trace components less than 1 wt%, its adaptability to measure every kind of element, and the flexibility to perform analyses in a diverse array of applications make the MiniFlex II+D/teX Ultra system stand out when compared to the conventional system.

Reference

(1) *The Rigaku Journal (English version)*, **27** (2011), No. 1, 20.